

Vinylketenes as Synthons for Bicyclic Systems

Inaugural-Dissertation

Submitted for the
degree of Doctor of Philosophy
to the Philosophical Faculty II
of the
University of Zürich

by

RIMA HUSTON-HACOPIAN
of Iran and the USA

approved by Prof. Dr. A. S. Dreiding

Zürich 1982
Zentralstelle der Studentenschaft

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Acknowledgement

I wish to thank Prof. A. S. Dreiding for his generous support and encouragement, which he provided throughout this work and Dr. M. Rey for his valuable and helpful suggestions and ideas.



To Alex and Leila,
my lovely children



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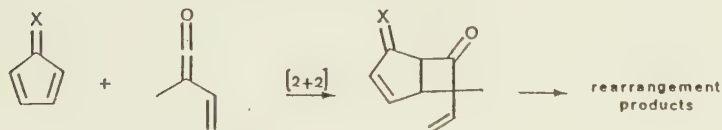
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A. Introduction

In this work the synthetic potential of the [2+2] cycloaddition of vinylketenes to cyclopentadiene and to 6,6-dimethylfulvene as well as the thermal and the acid-catalyzed rearrangements of the resulting cycloadducts are explored. It turns out that these reactions offer ready access to some ring systems, which so far have been available only with difficulty.



In section B, entitled Background, a comprehensive literature study on vinylketenes, on their reactions and on the rearrangements of vinylcyclobutane derivatives will be presented. The formulae there are designated with small letters starting from a, b, etc. in each subsection.

In section C the problems to be solved in this work are presented. The formulae are designated with capital letters.

Section D, entitled Own Work, contains the results obtained in this study and a discussion thereof. A possible application of

the studied reactions is presented here. The formulae are numbered consecutively with arabic numbers.

Section E contains the experimental details of this work; compounds have the same numbers as their formulae in section D.

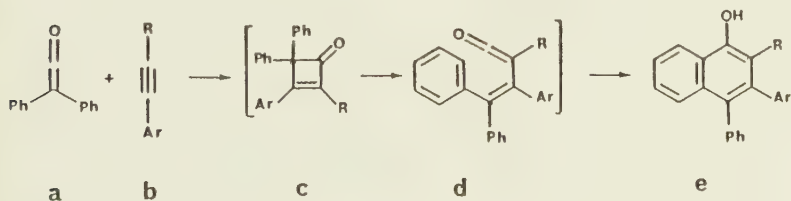
A short summary of the outcome of this work will be given in section F. The general formulae are designated with Roman numerals.

Section G lists the references to the literature.

B. Background

1. Vinylketenes

The occurrence of vinylketenes was first suggested in 1941 by Smith and Hoehn [1] in the reaction of diphenylketene a with arylacetylenes b. In this reaction the formation of α -naphthols e was explained by the initially formed, but not isolated, cyclobutenones c, which underwent a ring-opening reaction to the highly reactive vinylketenes d, the latter undergoing an electrocyclic reaction to yield e.

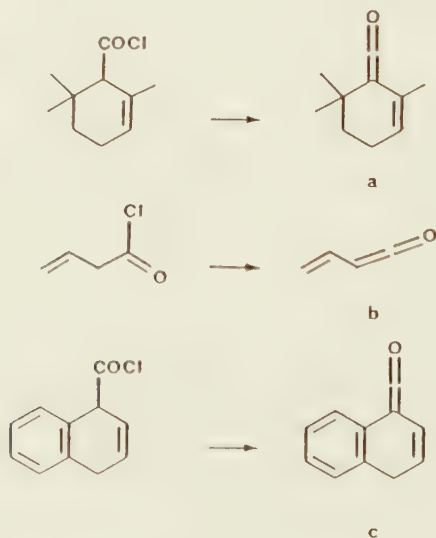


In the following paragraphs of this subsection the methods of generation of vinylketenes will be described, including the detection of the unstable vinylketene itself as well as the isolation of stable substituted vinylketenes. Subsequently the reactions of vinylketenes will be presented; they show that these reactive species can not only be trapped with nucleophiles [2] [3] [4] [5] [6] [7] [8] [9] [10] [11] [12] [13] [14], but that they also participate in many other reactions.

1.1. Methods of generation of vinylketenes

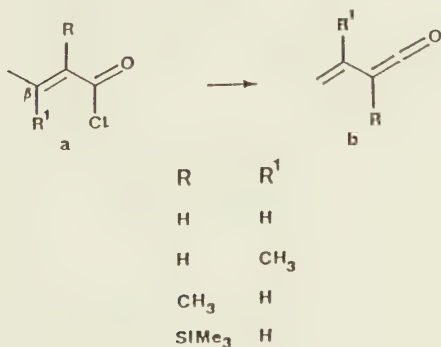
1.1.1. Dehydrochlorination of β,γ -unsaturated acid chlorides with base

The 1,2-elimination of hydrogen chloride from β,γ -unsaturated acid chlorides with triethylamine yielded vinylketenes, one of which, namely a could even be isolated as a stable compound and characterized [15]. Others such as vinylketene b itself [16] was trapped with olefins [16] and acetylenes [17] and the derivative c with acetylenes [17].



1.1.2. Dehydrochlorination of α,β -unsaturated acid chlorides with base

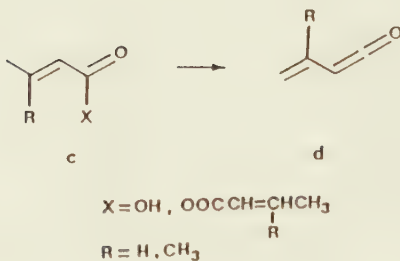
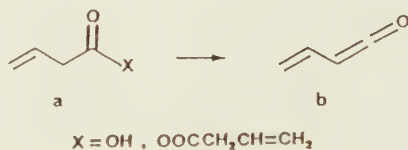
Several vinylketenes b have also been generated by 1,4-elimination of hydrogen chloride with either triethylamine or trimethylamine from α,β -unsaturated acid chlorides a which carry a CH_3 -group in the β position [3] [4] [18] [19] [20] [21]. The vinylketene b ($\text{R} = \text{SiMe}_3$ and $\text{R}' = \text{H}$) was sufficiently stable to be isolated [20].



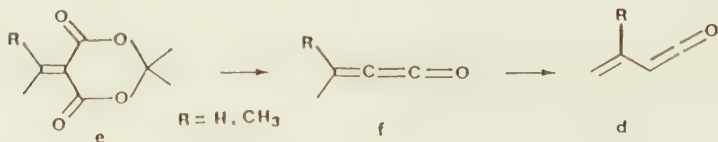
1.1.3. Pyrolysis of unsaturated carboxylic acid derivatives and of alkylidenemalonates

In the same way as ketenes were prepared by the pyrolysis of carboxylic acid derivatives, vinylketenes b and d have been generated in the gas phase by 1,2-elimination of HX from 3-butenic acid (at 477°) and 3-butenic acid anhydride (at 500°) (a, $\text{X}=\text{OH}$ and 3-butenate) [14]] [22] and by 1,4-elimination of HX from

α,β -unsaturated carboxylic acid derivatives at 500-550° (c, X=Cl, OH and 2-butenolate) [22].

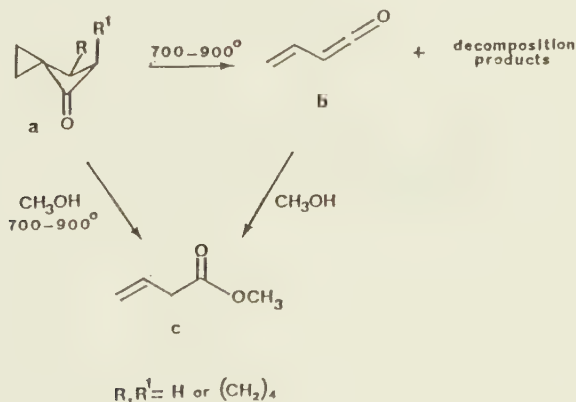


Short-path gas phase pyrolysis of alkylidene malonates e at 490° produces alkylideneketenes f which rearrange in the heating zone to the thermodynamically more stable vinylketenes d [22].



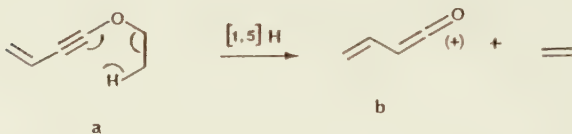
1.1.4. Flash thermolysis of spiro[2,3]hexan-4-ones

In the flash thermolysis ($700-900^{\circ}$) of spiro[2,3]hexan-4-ones a, vinylketene b was generated by the elimination of $RCH=CHR^1$. The presence of b was identified by treating the pyrolysate with methanol or carrying out the pyrolysis in a flow of methanol which gave 3-butenolate c [7], together with decomposition products.



1.1.5. Gas-phase thermal decomposition of an en-yne-ether

Ionization of the en-yne-ether a at 70 eV produced the m/e 68 ion namely $[C_4H_4O]^+$, which was assigned to vinylketene b ion [23].



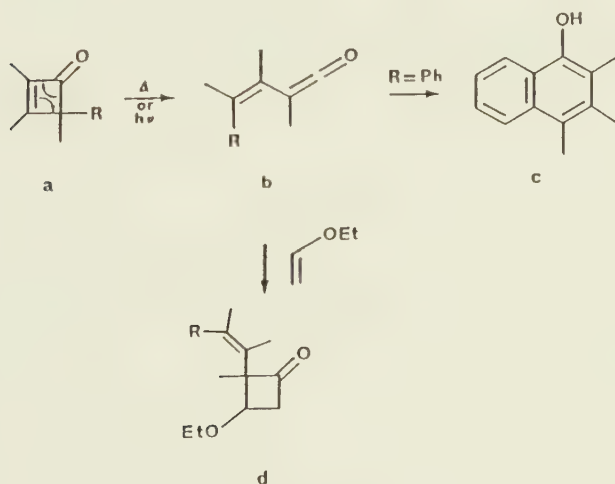
The formation of b was rationalized by a fragmentation involving a [1,5]-hydrogen shift as shown in a.

1.1.6. Ring-opening reactions

Three major ring-opening reactions have been found to produce vinylketenes:

1.1.6.1. From cyclobutenones

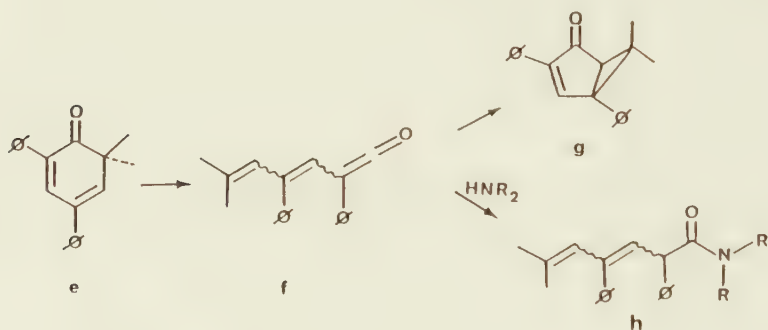
Cyclobutenones a have been suggested [1] and shown to undergo electrocyclic ring opening, both thermally [10][12] and photochemically [10], to yield vinylketenes b.



With $R = Ph$, the reaction proceeded to α -naphthols c (see Section B.1) [10][12]; with $R = H$ or CH_3 , the formation of b could be shown by [2+2] cycloaddition to an enol ether to d [10].

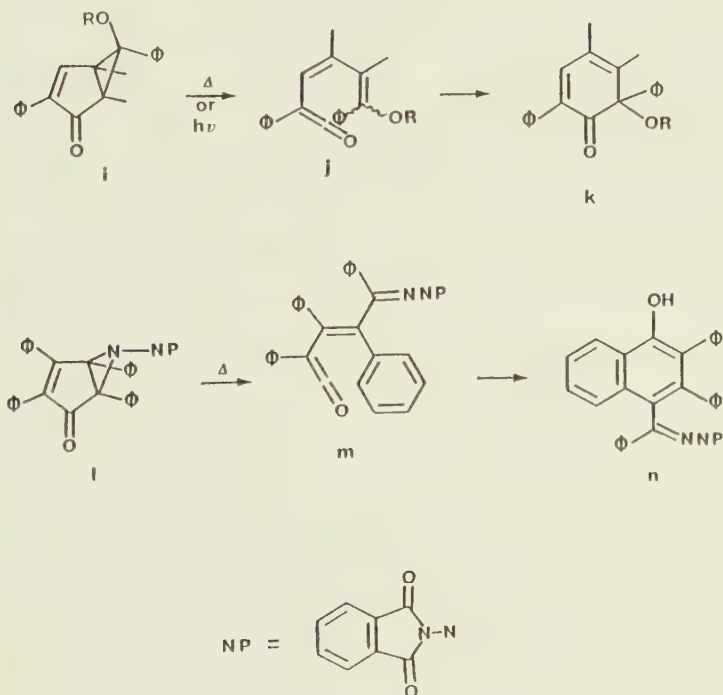
1.1.6.2. From cyclohexadienones

In the photochemical conversion of 2,4-cyclohexadienones e to bicyclo[3.1.0]hexenones g, substituted vinylketenes f have been postulated as intermediates [6] [13] [24]. When the reaction was carried out in the presence of secondary amines the substituted amides h were obtained [6].



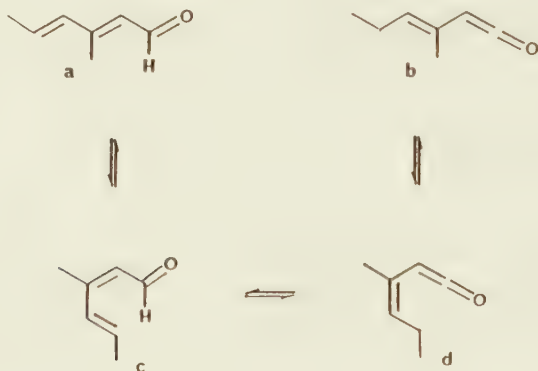
1.1.6.3. From bicyclo[3.1.0]hexenones

The substituted vinylketenes j and m were postulated in the thermal (at 110-140°) and photochemical ring opening reaction of the bicyclo[3.1.0]hexenone i and in the thermal ring opening of the 6-azabicyclo[3.1.0]hexenone l; they underwent immediate ring closures to 2,4-cyclohexadienones k [11] [25] and to α -naphthols n [26], respectively.



1.1.7. [1,5] Sigmatropic hydrogen shift in $\alpha,\beta,\gamma,\delta$ -unsaturated aldehydes

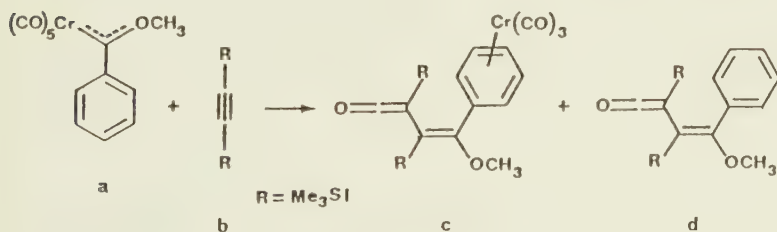
Vapor-phase pyrolysis (at 600⁰) of 2,4-pentadienals a has been demonstrated to lead to vinylketenes b (among other products) by a [1,5] H shift [5][9]. These reactions are reversible and were used to equilibrate cis and trans isomers of the 2,4-pentadienal a/c as well as those of the vinylketenes b/d [9]. The formation of vinylketenes b and d were shown in the IR and ¹H-NMR. spectra of the mixture.



1.1.8. By carbene insertion from metal carbonyl-carbene complexes

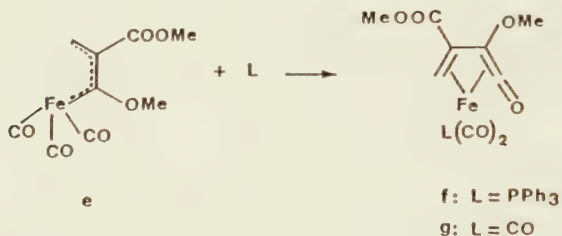
1.1.8.1. Chromium pentacarbonyl

Pentacarbonyl[methoxy(phenyl)carbene]chromium a reacts with bis(trimethylsilyl)acetylene b at 50° to yield vinylketene tri-carbonyl chromium complex c as well as the free vinylketene d in 52% and 20% yields, respectively [27].

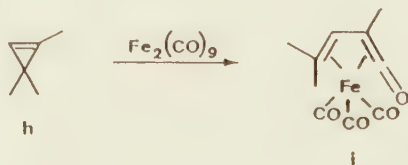


1.1.8.2. Iron pentacarbonyl complexes

In the reaction of η^3 -vinylcarbene iron carbonyl e with triphenylphosphine or carbon monoxide η^4 -vinylketene iron complexes f and g were obtained, respectively [28].

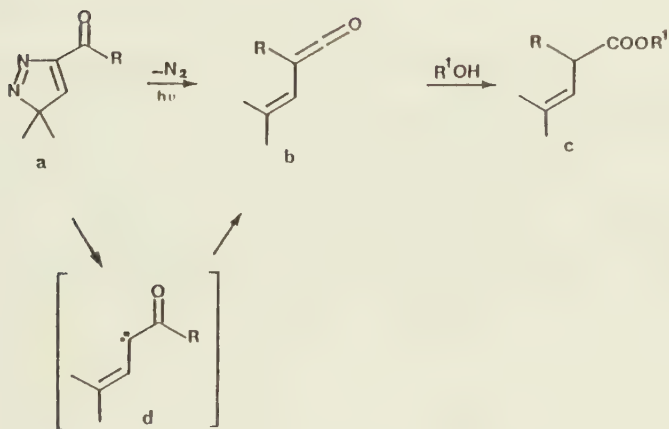


The substituted cyclopropene h was observed to undergo a ring opening reaction with iron carbonyl to yield the vinylketene iron tricarbonyl complex i, a crystalline compound, stable at RT. [29].



1.1.9. Nitrogen elimination from 5-acyl pyrazolenines

Photolysis of 5-acyl pyrazolenines a produced vinylketenes b, which were trapped with an alcohol to give the esters c [8].



The reaction was explained via nitrogen elimination to give the carbene d with a subsequent 1,2 migration of the R group to b.

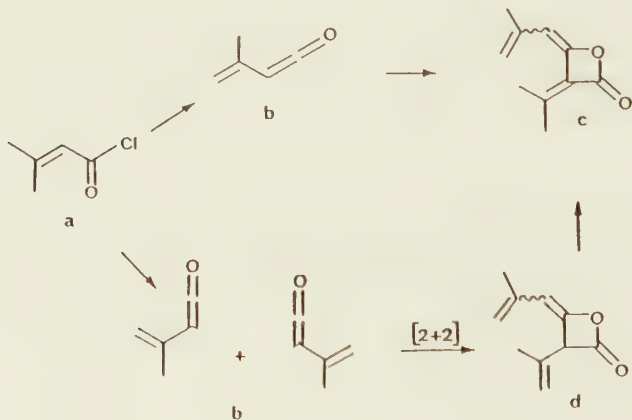
1.2. Reactions of vinylketenes

Aside from the addition reactions of nucleophiles, mainly used to prove their existence as intermediates (see Section B.1), vinylketenes take part in cycloadditions, as will be reviewed below.

1.2.1. Dimerization

1.2.1.1. Formation of β -lactones

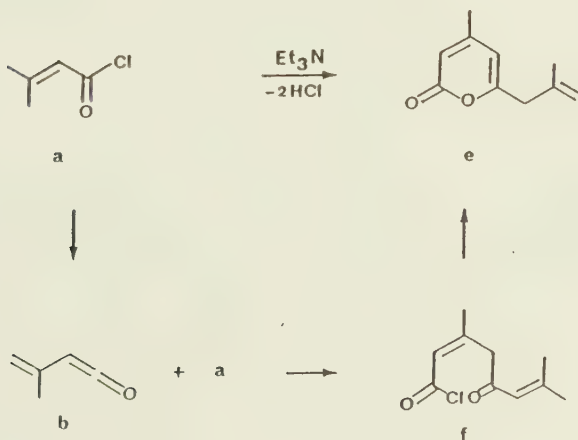
In one of the earliest works on vinylketenes, Payne [18] reported the dimerization of isopropenylketene b, generated from α,β -unsaturated acid chloride a with trimethylamine, to the β -lactone c in acetone solution.



This dimerization reaction could be interpreted as a [2+2] cycloaddition in which the carbonyl portion of one ketene function reacts with the double bond portion of another ketene function to d, followed by a double bond migration to give c.

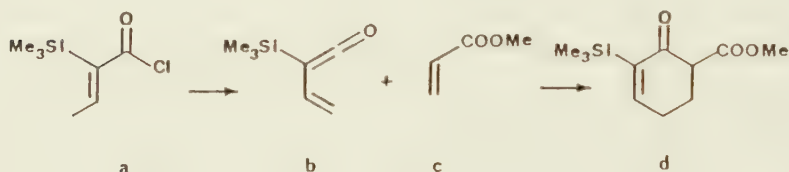
1.2.1.2. Formation of 2-pyrones

This formal [4+2] dimerization of two molecules of vinylketenes b leading to 2-pyrones d [19], probably proceeds as follows: First a molecule of the vinylketene b is generated in the usual way from the acid chloride a; it then reacts with another molecule of the $\alpha,3$ -unsaturated acid chloride a to give the unsaturated keto-acid chloride f, which finally cyclizes with the loss of HCl to the pyrone e.

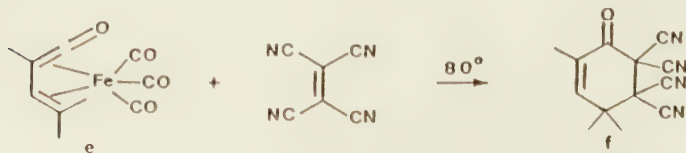


1.2.2. [4+2] Cycloaddition

The stable α -silyl-vinylketene b, prepared by 1,4-elimination of HCl from the acid chloride a was shown to be inert to [2+2] cycloaddition. However, it underwent Diels-Alder reactions with dienophiles c to give substituted cyclohexenones d [20].



Similarly, a vinylketene-iron carbonyl complex e reacted with tetracyanoethylene in boiling benzene in a [4+2] fashion to give the 1:1 adduct f of the free vinylketene [29].

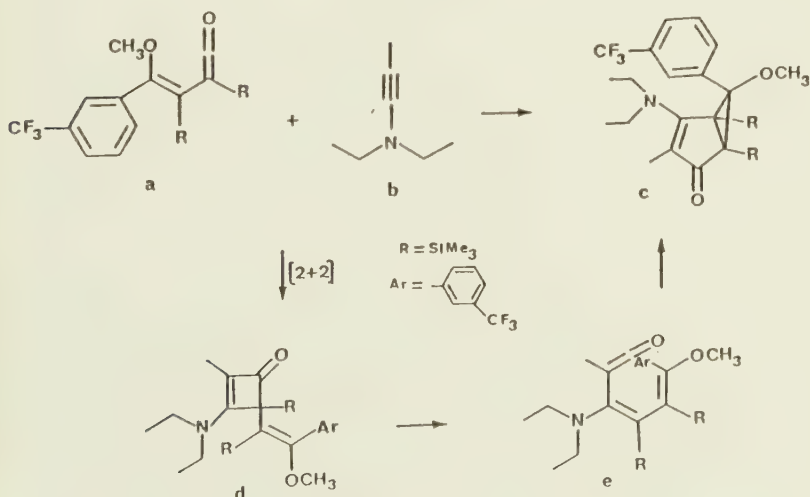


1.2.3. [2+2] Cycloaddition

Analogous to ketenes, vinylketenes undergo [2+2] cycloadditions to olefins and to acetylenes. Because of their relevance to this work they will be reviewed in this section in somewhat more detail:

1.2.3.1. To ynamines

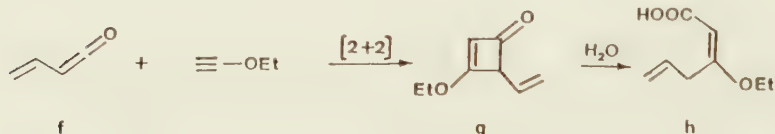
In the reaction of bis-trimethylsilylated vinylketenes a with ynamine b, the bicyclo[3.1.0]hexenone c was obtained [30]. The unusual formation of this ring system was rationalized by an ini-



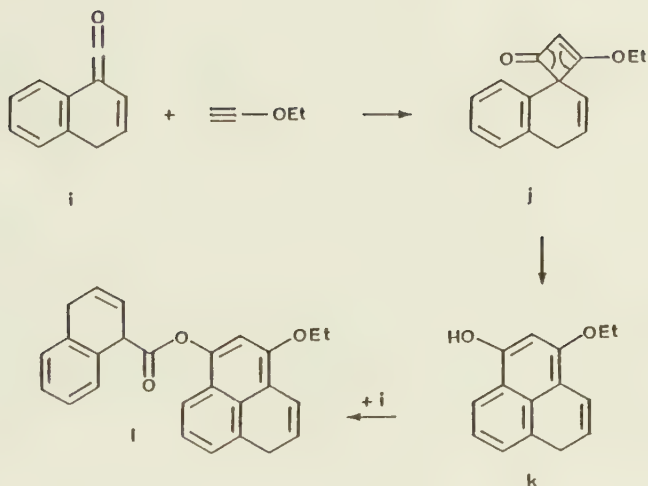
tial [2+2] cycloaddition to the cyclobutenone d, subsequent ring opening reaction to the conjugated vinylketene e, and final cyclization to c (see Section B.1.1.6.2 for a similar transformation).

1.2.3.2. To alkoxy acetylenes

Reaction of vinylketenes and acetylenes yielded cyclobutenones, which rearranged readily to other carbon skeletons [17]. For instance, vinylketene itself f (see Section B.1.1.1 for the preparation) reacted with ethoxyacetylene to the cyclobutenone g, which was readily hydrolyzed to the hexadienoic acid h.

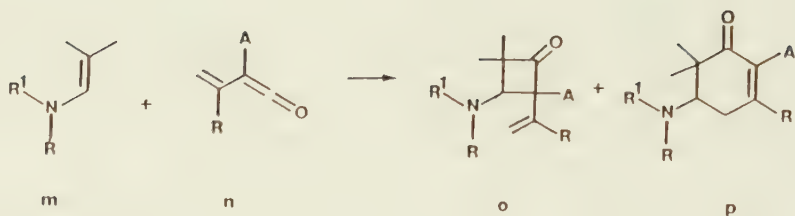


In another example of the same work, the vinylketene i combined with ethoxyacetylene; the primary product, presumably the cyclobutenone j, rearranged further, presumably via another vinylketene (compare Section B.1.1.6.1), to give the α -naphthol k, which finally reacted with another molecule of i to yield the polycyclic ester l.

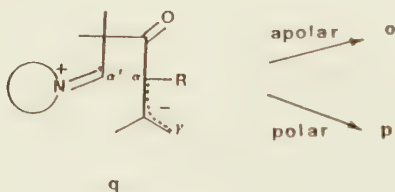


1.2.3.3. To enamines

Enamines m and vinylketenes n have been shown to undergo [2+2] and/or [4+2] cycloadditions to give mixtures of 3-amino-2-vinylcyclobutanones o and/or 5-amino-cyclohexenones p [31] [32]. The product distribution depends on the enamine, markedly on the solvent used and also on the substituent A on the vinylketene n. For instance, in hexane and using the morpholinoenamine (m, $\text{RR}^1 = (\text{CH}_2)_2\text{O}(\text{CH}_2)_2$), the cycloaddition with methyl-vinylketene (n, $\text{A} = \text{CH}_3$, $\text{R} = \text{H}$) gave mainly the vinylcyclobutanone o. Using the pyrrolidinoenamine (m, $\text{R}, \text{R}^1 = (\text{CH}_2)_4$) and CH_2Cl_2 as the solvent, the reaction of n yielded only p [32].

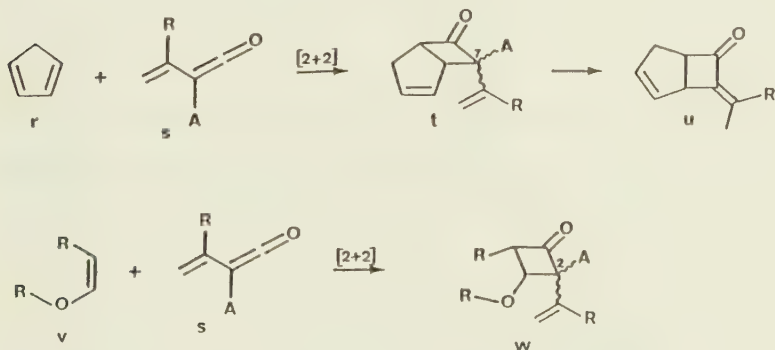


A unified mechanism explaining the formation of both products o and p involves the dipolar intermediate q which cyclizes to o in an apolar solvent (α' - α closure) and to p in a polar solvent (α' - γ closure) [32].



1.2.3.4. To olefins and enolethers

Vinylketenes s, generated in situ from α,β -unsaturated acid chlorides, undergo [2+2] cycloaddition with cyclopentadiene r in a regiospecific manner to yield stereoisomeric 7-substituted vinylbicyclo[3.2.0]hept-2-en-6-ones t [16][19][21]. According to the well documented ketene cyclopentadiene cycloaddition [33], this [2s+2a] cycloaddition proceeds to give preferentially bicycloheptenones t with the bulkier substituent in the sterically more crowded 7-endo position. In those cases where A = H and R = H or CH₃, the vinyl double bond migrates into conjugation to give the bicyclic ketone u. Vinylketenes s also react with enol ethers v to give mixtures of diastereoisomeric vinylcyclobutanones w [10][18] [34].

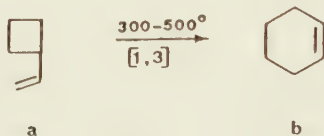


1.3. Rearrangement of vinylcyclobutane derivatives

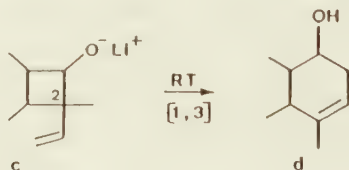
In this section the sigmatropic rearrangement of vinylcyclobutane derivatives will be discussed, with emphasis on the rearrangement of 2-vinylcyclobutanones.

1.3.1. Rearrangement of vinylcyclobutanes and vinylcyclobutanols.

Vinylcyclobutanes a have been shown to suffer a [1,3] sigmatropic rearrangement at elevated temperatures to yield cyclohexenes b [35].

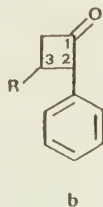


In a similar way, lithium salts of 2-vinylcyclobutanols c rearranged already at RT. to 3-cyclohexenols d [21]. The acceleration of this [1,3] sigmatropic shift has its analogy in the anionic oxy-Cope rearrangement.



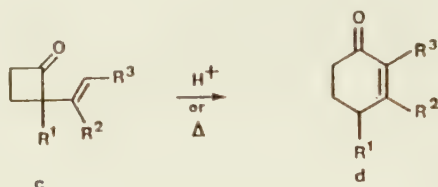
1.3.2. Rearrangement of 2-vinylcyclobutanones

2-Vinylcyclobutanones a and 2-arylcylobutanones b, in which the vinyl group is incorporated in the aromatic ring, have been shown to undergo several types of rearrangements, the driving force apparently being the relief of the strain in the four-membered ring. In both cases, a and b, two bonds may break: cleavage of the C(1),C(2)-bond entails an acyl migration and that of C(2),C(3)-bond an alkyl migration. The latter occurs only if the R group is a cation stabilizing substituent, such as phenyl, vinyl or an OR group. The following subsections will deal with three types of reactions which involve the cleavage of one of these two bonds in a or in b.

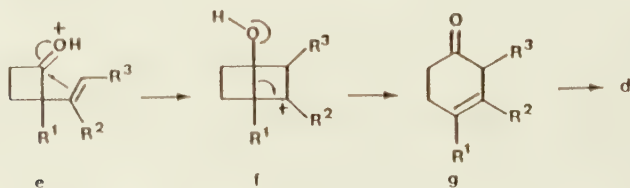


1.3.2.1. [1,3] Acyl migration

When 2-vinylcyclobutanones c were thermolyzed (330°) [36] or treated with methanesulfonic acid [37] 2-cyclohexenones d were obtained. A [1,3] acyl migration for both the acid catalyzed and the thermal rearrangement was given as an explanation for the course of this reaction.

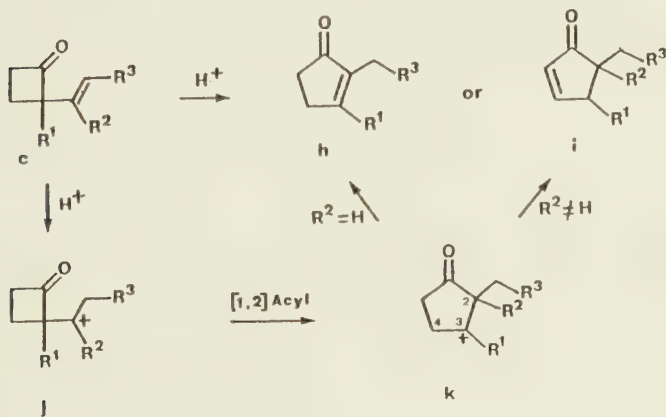


As a reasonable mechanism for the acid catalyzed process, the authors postulated the protonation of the carbonyl group to e, followed by the attack of the double bond at the carbonyl carbon atom, resulting in the bicyclic cation f which opened to g; migration of the double bond into conjugation by the action of the acid yielded d [37].



1.3.2.2. [1,2] Acyl migration

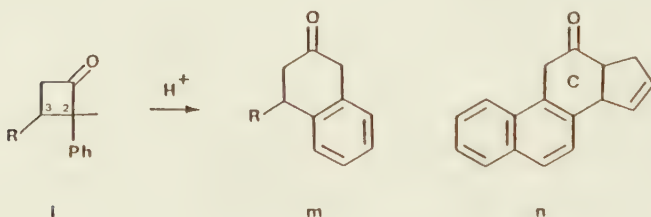
2-Alkyl-2-vinylcyclobutanones c (R^1 = alkyl) in some cases underwent [1,2] acyl migration when subjected to methanesulfonic acid. The products were substituted cyclopentenones h (when R^2 = H) or i (when R^2 = alkyl) [37].



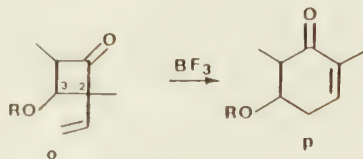
The mechanism presented by the authors involved initial protonation of the side chain double bond to yield the cation j; this was followed by a [1,2] acyl migration (involving C(1),C(2)-bond), leaving the positive charge on C(3) of k. Finally the loss of a proton from C(2) when $R^2 = H$ yielded cyclopentenone h, whereas the loss of a proton from C(4) (R^2 = alkyl), followed by the migration of the double bond into conjugation, afforded the cyclopentenone i.

1.3.2.3. [1,3] Alkyl migration

In the acid catalyzed (CF_3COOH) rearrangement of 2-arylcyclobutanones l which bear a cation stabilizing substituent on C(3) (i.e. R = phenyl, vinyl or an alkoxy group), a [1,3] alkyl migration (involving the C(2),C(3)-bond) has been observed, leading to substituted arylcyclohexanones m [38]. This rearrangement was exploited in building up ring C of a skeleton n, similar to a steroid hormone [38].



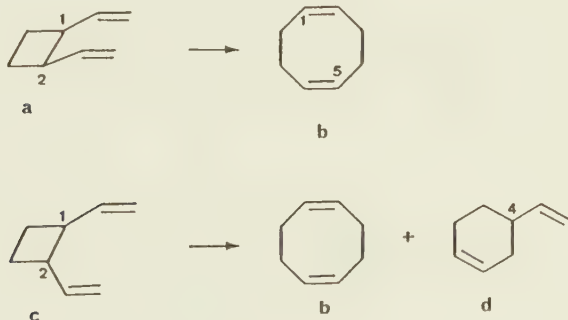
Similarly, when the cycloadducts of vinylketenes and enoethers o were treated with boron trifluoride, they rearranged to yield 2-cyclohexenones p [34].



Here the substituent on C(3) is an oxygen atom, which again could enhance the migrating capacity of the C(3),C(2)-bond in o.

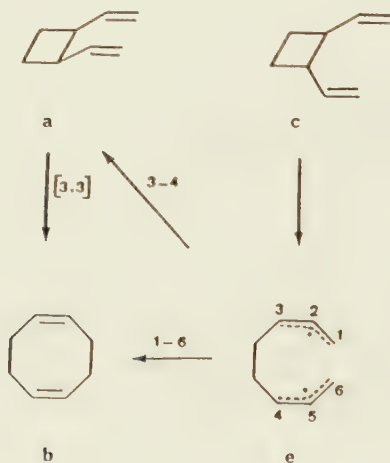
1.3.3. Rearrangement of divinylcyclobutane derivatives

In 1958 Vogel [39] reported the facile Cope rearrangement of *cis*-1,2-divinylcyclobutane a at 120° to 1,5-cyclooctadiene b in 91% yield. *Trans*-1,2-divinylcyclobutane c was also shown to rearrange, but at somewhat higher temperatures (150-200°), to 1,5-cyclooctadiene b ([3,3] product) and 4-vinylcyclohexene d ([1,3] product) in 30% and 70% yields, respectively [40].



Other studies [40] [41] [42] showed that increasing the substitution on C(1) and C(2) of the four-membered ring, as well as on the vinyl groups of *trans*-1,2-divinylcyclobutane led to mixtures, the [3,3] product being the minor component. There are different views regarding the mechanism of the [3,3] sigmatropic rearrange-

ment of trans-1,2-divinylcyclobutanes, the rearrangement of the cis-isomers always considered to be a concerted process. Berson and coworkers [42] proposed two pathways for the rearrangement of trans-1,2-divinylcyclobutane c to 1,5-cyclooctadiene b : 1) an indirect mechanism requiring prior epimerization of c to cis 1,2-divinylcyclobutane a by way of a diradical intermediate e, followed by the concerted [3,3] rearrangement of a to b and 2) a direct mechanism proceeding from the diradical e directly to the rearrangement product b.

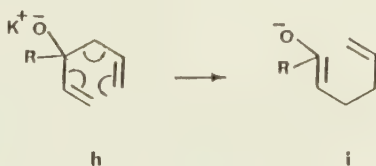


Other authors favored for the trans-1,2-divinylcyclobutanes a mechanism in which the common diradical intermediate corresponding to e would lead to the [3,3] as well as the [1,3] rearrangement products [40][41].

The term oxy-Cope rearrangement was first proposed by Berson and Jones [43] who prepared Cope systems f in which a hydroxyl group was attached to C(3). Pyrolysis (250-320°) of these systems gave δ,ϵ -unsaturated ketones g.



Evans and Golob [44] used the potassium alkoxides h, instead of the alcohols f, and observed a tremendous rate acceleration of the oxy-Cope rearrangement. This rearrangement gives the enolate anion of the ketone i which can be directly used for further synthesis.



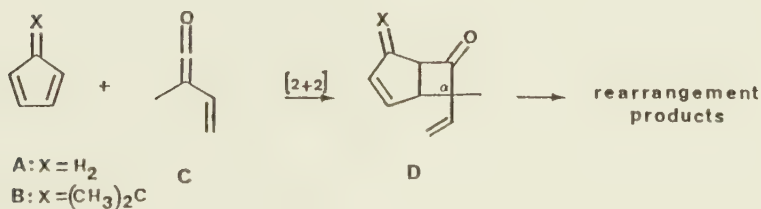
Of the many oxy-Cope rearrangements reported in the literature, only one involved a 1,2-divinylcyclobutanol system; it was studied by Kahn [45] who showed that the anionic oxy-Cope rearrange-

ment of a divinylcyclobutanol j proceeded at 55° via its potassium alkoxide to give the strained eight-membered unsaturated ketone k in 35% yield.



C. Problem presentation

Vinylketenes (C) have been shown to undergo a number of interesting reactions. However, prior to the onset of this work, little had been done on the [2+2] cycloaddition of vinylketenes to olefins. Only three cases were known of additions to cyclopentadiene (A) and no case of an addition to 6,6-dimethylfulvene (B). No work had been done on the rearrangement of the resulting cycloadducts (D).



The cycloadducts D contain a cyclobutane ring which - due to its internal strain - has been known to suffer rearrangements. They also contain two or three double bonds in positions which are known to enhance rearrangements involving a cyclobutane bond, namely a vinyl substituent alpha to the carbonyl group and a Cope system.

The questions we posed ourselves in the present work were: 1)
Is the cycloaddition of vinylketenes (readily generated in situ)

to cyclopentadiene (A) a general reaction? 2) Do vinylketenes C also add to 6,6-dimethylfulvene (B)? 3) What kind of rearrangements do the cycloadducts (D) undergo a) thermally and b) under acid catalysis?

With this investigation we wished to explore the potential usefulness of these reactions for the synthesis of terpenoid natural products. One possible synthetic scheme is outlined in Section D.4, p. 60.

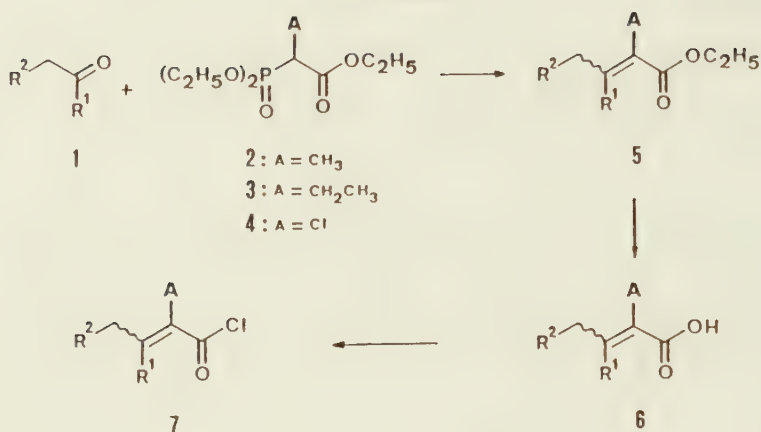
D. Own work

1. Synthesis of 7-vinylbicyclo[3.2.0]hept-2-en-6-ones.

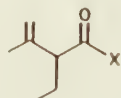
1.1. Preparation of α,β -unsaturated acid chlorides (7).

The α -alkyl- and α -chloro- α,β -unsaturated acid chlorides (7), required as alkyl-vinylketene and chloro-vinylketene precursors, were prepared as follows (see Scheme 1): Wittig-Horner condensation of the carbonyl compounds 1 with triethyl 2-phosphonopropionate (2), triethyl 2-phosphonobutyrate (3) [46] or triethyl 2-chloro-2-phosphonoacetate (4) [47] afforded the α,β -unsaturated esters 5, which were saponified in crude form to give the α,β -unsaturated acids 6, most of them previously available from other methods [48] [49] [50] [51] [52] [53] [54] [55]. Conversion of the unsaturated acids 6 to the corresponding unsaturated acid chlorides 7 was accomplished with SOCl_2 ; the overall yields of the acid chlorides 7 from the carbonyl compounds 1 were 30-59%. No effort was made to control the stereospecificity of the Wittig condensations 1 + 2, 3 or 4 $\longrightarrow$ 5, since the stereogenic double bond in 5, 6 and 7 was destined to be moved away in the formation of the vinylketenes 8 from 7. The acids 6b and 6f and their chlorides 7b and 7f were obtained as the pure (E)-isomer and (Z)-isomer, respectively (δ H-C(3), for b = 6.93 and 7.19 ppm and for f = 7.31 and 7.37 ppm, cf. [56]). All the other acids 6 and their acid chlorides 7, containing a stereogenic double bond, appeared as mixtures of their (E)- and (Z)-isomers (Scheme 1).

Scheme 1



	R ¹	R ²	A	Yield (7)	(E):(Z)-ratio
a *	H	H	CH ₃	93% [19]	100:0
b	H	CH ₃	CH ₃	58%	100:0
c	CH ₃	H	CH ₃	59%	
d	CH ₃	H	CH ₂ CH ₃	58%	
e	-(CH ₂) ₃ -		CH ₃	41%	
f	H	H	Cl	45%	0:100
g	H	CH ₃	Cl	31%	80:20
h	CH ₃	H	Cl	30%	
i	CH ₃ CH ₂	H	Cl	30%	60:40
j	-(CH ₂) ₄ -		Cl	59%	



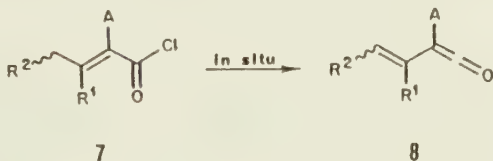
9: X=OH
 10: X=Cl

* Prepared from commercially available (E)-2-methyl-2-butenoic acid

The acid 6d and its chloride 7d were accompanied by an equal amount of their β,γ -double bond isomers 9 and 10.

1.2. [2+2] Cycloaddition of vinylketenes (8) to cyclopentadiene (11) and to 6,6-dimethylfulvene (12).

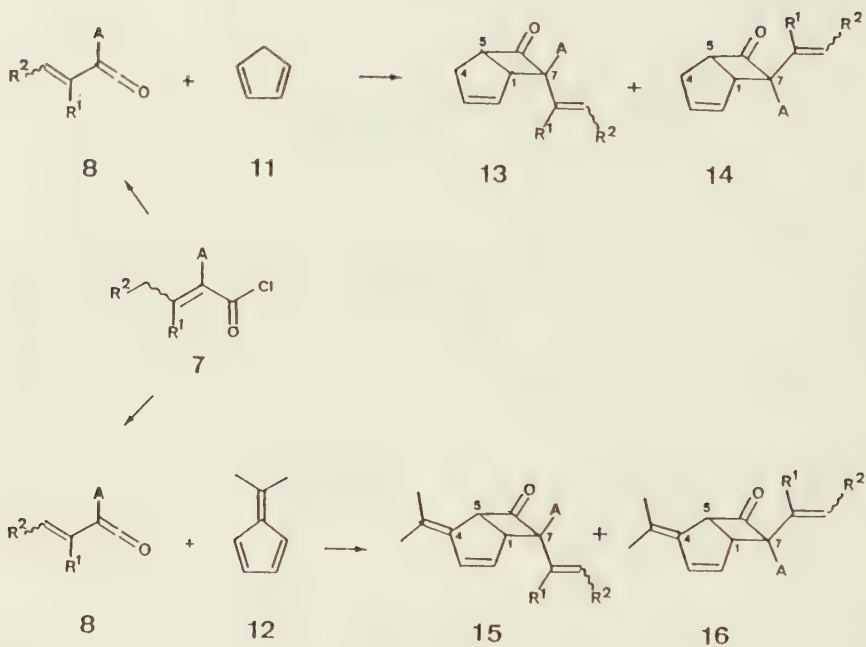
The vinylketenes 8, generated from the five α -alkyl acid chlorides 7a - 7e and from the four α -chloro acid chlorides 7f, 7g, 7h and 7j with triethylamine, were added to cyclopentadiene (11) to give the stereoisomeric 7-vinyl substituted bicyclo[3.2.0]-hept-2-en-6-ones 13 and 14. In the same way, the vinyl-



ketenes 8, generated from (E)-2-methyl-2-butenoyl chloride (7a) [19] and from the α -chloro acid chlorides 7f and 7i with triethylamine reacted with 6,6-dimethylfulvene (12) to give the stereoisomeric 7-vinyl substituted 4-isopropylidenebicyclo[3.2.0]-hept-2-en-6-ones 15 and 16. The present examples of 13/14 and of 15/16, together with their yields of formation (10-84%), are shown in Table 1.

[2+2] Cycloadditions of this kind are fully regiospecific, so that two double bonds in the product turn out to be separated by two saturated carbon atoms. However, two stereoisomers may be formed, one with the vinyl group in the endo- (13 and 15) and the

Scheme 2



	R^1	R^2	A	
<u>a</u>	H	H	CH_3	[19]
<u>b</u>	H	CH_3	CH_3	
<u>c</u>	CH_3	H	CH_3	
<u>d</u>	CH_3	H	CH_2CH_3	
<u>e</u>	$-(CH_2)_3-$		CH_3	
<u>f</u>	H	H	Cl	
<u>g</u>	H	CH_3	Cl	
<u>h</u>	CH_3	H	Cl	
<u>i</u>	CH_3CH_2	H	Cl	
<u>j</u>	$-(CH_2)_4-$		Cl	

other with vinyl group in the exo-position (14 and 16) (see Scheme 2). The ratio of these stereoisomers (as shown in Table 1) depends on the relative size of the two substituents on the ketene function. Thus increasing the size difference between these two substituents leads to a greater preponderance of the cycloadduct with the larger substituent in the 7-endo position, an effect which has been observed [33] in other ketene-cyclopentadiene cycloadditions. The evidence for the configurational assignments will be given in Section D.1.3.

The two C(7)-stereoisomers of the cycloadducts 13a/14a, 13f/14f, 13g/14g, 15a/16a and 15f/16f were not separated; the vinyl-endo/vinyl-exo (13:14 and 15:16) isomer distribution was determined by gas-liquid chromatography and verified by the relative intensities of the characteristic ^1H -NMR.-signals. The two C(7)-stereoisomers of the cycloadduct 13d/14d were separated from each other.

A further stereogenic center is found in the double bond of the side chain of 13b/14b and of 13g/14g. In the former case, the stereoisomers were separated and both shown to contain an (E)-configured double bond by the trans coupling constant ($J = 15.5 \text{ Hz}$) between C(1') and C(2') in their ^1H -NMR. spectra. In the latter case, however, the stereoisomers were not separated, so that it is not possible to say whether their propenyl groups have the (E)- or (Z)-configuration or whether they are mixtures of double bond isomers.

Table 1: Summary of results on the [2+2] cycloaddition of vinylketenes
(8) to cyclopentadiene (11) and to 6,6-dimethylfulvene (12)

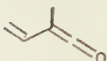
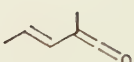
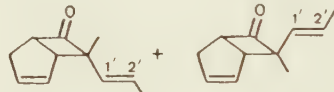
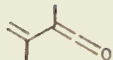
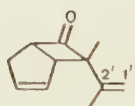
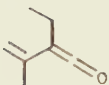
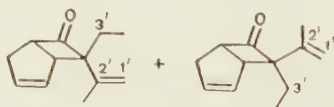
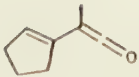
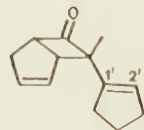
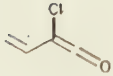
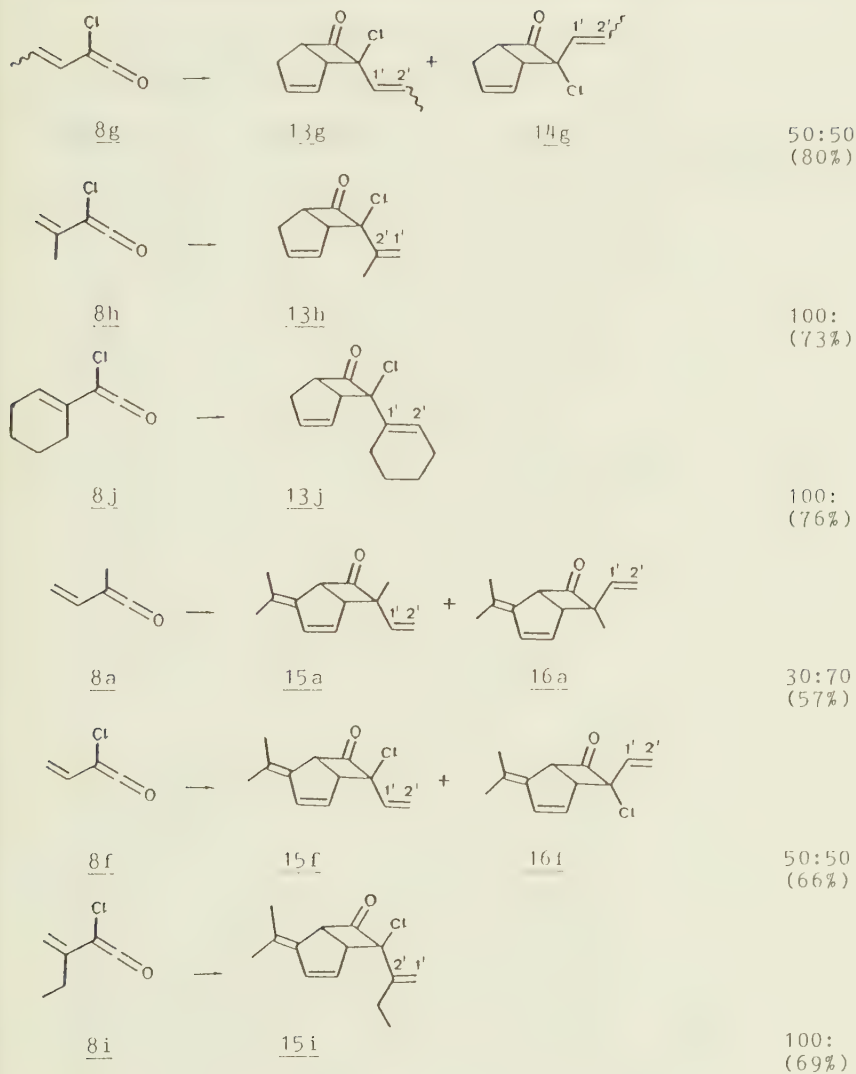
<u>Vinylketenes</u>	<u>Cycloadducts</u>	<u>Isomer ratio</u> <u>endo-vinyl:exo-vinyl</u> (yield)
 8a	 13a + 14a	30:70 (77%)
 8b	 13b + 14b	40:60 (33%)
 8c	 13c	100: (28%)
 8d	 13d + 14d	100:10 (10%)
 8e	 13e	100: (74%)
 8f	 13f + 14f	50:50 (84%)

Table 1 (continued):



1.3. Configurational assignment of the vinylketene-cycloadducts

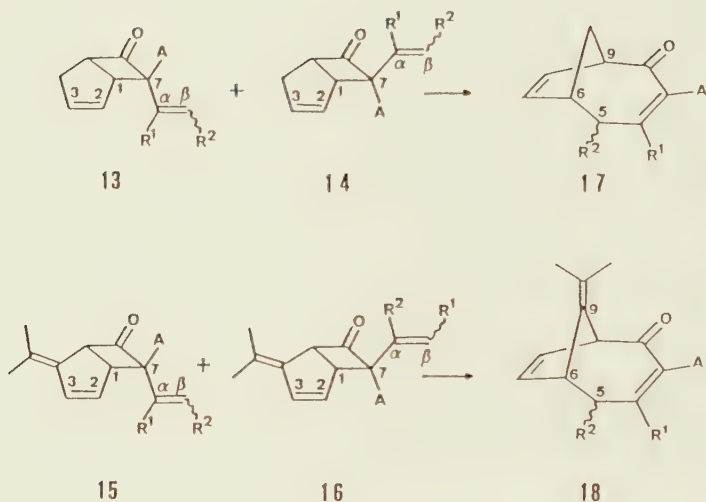
In the chloro-vinylketene cyclopentadiene cycloadducts 13/14 ($A = Cl$), the configuration at C(7) was assigned on the basis of the 1H -NMR.-signals for H-C(5), which always occurs at lower field when the chlorine atom at C(7) is in the *exo*- (cis to H-C(5): 4.08-4.27 ppm) rather than in the *endo*-position (trans to H-C(5): 3.88-3.90 ppm) [33]. The same effect can be used with the chloro-vinylketene-dimethylfulvene cycloadducts 15/16 ($A = Cl$), even though their H-C(5) signals occur further downfield (by about 0.5 ppm) due to the additional (exocyclic) double bond at C(4).

In the alkyl-vinylketene-cyclopentadiene cycloadducts 13/14 ($A = CH_3$ or CH_2CH_3) and alkyl-vinylketene-6,6-dimethylfulvene cycloadduct 15a/16a, the configuration at C(7) was derived from the larger chemical shift difference of the *exo*-methyl group in CCl_4 and in C_6D_6 solution ($\Delta\delta_{CCl_4-C_6D_6}$) as compared to the *endo*-methyl group, a criterion previously employed for a series of 7,7-dialkyl substituted bicycloheptenones [57] including 13a/14a. Thus the $\Delta\delta_{CCl_4-C_6D_6}$ is 0.18-0.26 ppm for 13 (*exo*-methyl) and 0.01-0.08 ppm for 14 (*endo*-methyl). In the case of 13d/14d, which carry an ethyl rather than a methyl group at C(7), the $\Delta\delta_{CCl_4-C_6D_6}$ value for the (diastereotopic) $-CH_2-C(7)$ exhibited a similar difference: 0.42 and 0.31 ppm in 13d (*exo*-methylene) and 0 and 0.1 ppm for 14d (*endo*-methylene). Furthermore, the 1H -NMR.-signals (in $CDCl_3$) due to $CH_3-C(7)$ or $-CH_2-C(7)$ occurred at lower field by more than 0.3 ppm in the vinyl-*endo*-isomers (13a, b, c, d, e and 15a) than in the vinyl-*exo*-isomers (14a, b, d and 16a).

2. Thermal rearrangement of the vinylketene cycloadducts

The cycloadducts 13 to 16 contain a Cope system, the carbon atoms C(3), C(2), C(1), C(7), C(α), C(β) (see Scheme 3). In the vinyl-endo-isomers 13 and 15, this system is fixed in a syn-conformation at C(1), C(7); in the vinyl-exo-isomers 14 and 16, however, in an anti-conformation. Heating nine of these cycloadducts 13a/14a, 13e, 13f/14f, 13g/14g, 13h, 13j, 15a/16a, 15f/16f and 15i, either in xylene (145°) or neat (160° or 190°), yielded the substituted bicyclo[4.2.1]nona-3,7-dienones 17 and 18 (see Scheme 3) in 48-90% yields (excepting 17g), as shown in Table 2. The low yield of 17g (6%) is due to formation of by-products, which were not examined closely at this point.

Scheme 3



	R^1	R^2	A
a	H	H	CH_3
e	$-(\text{CH}_2)_3-$		CH_3
f	H	H	Cl
g	H	CH_3	Cl
h	CH_3	H	Cl
i	CH_3CH_2	H	Cl
j	$-(\text{CH}_2)_4-$		Cl

A comparison of the yields of 17a and 18a with the stereoisomer ratios of the starting materials 13a/14a and 15a/16a, respectively, shows that the products of the Cope-rearrangement are obtained not only from the vinyl-endo- (13 and 15) but also from the vinyl-exo-isomers (14 and 16). Gas chromatographic monitoring of the thermolysis mixture in the case of 13a/14a showed that the vinyl-endo-isomer (13a) disappeared about three times as fast as the vinyl-exo-isomer (14a).

Three of the rearrangement products, 17e, 17g and 17j, carry a substituent at C(5), making C(5) a stereogenic center (numbering corresponds to formula 17). However, in all three cases only one diastereoisomer was found, 17e and 17j being formed from precursors (13e and 13j) with an (E)-configured double bond (fixed by the five- and six-membered ring) in the C(7) vinyl substituent.

On standing at RT. 17j lost HCl to form the trienone 19. The detailed course of the latter transformation was not examined.

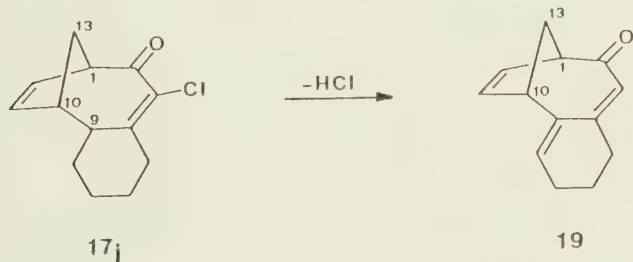


Table 2: Summary of results on the thermal rearrangement of
vinylketene cycloadducts

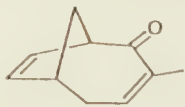
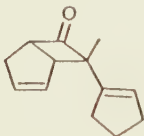
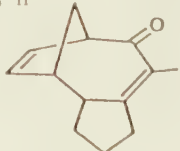
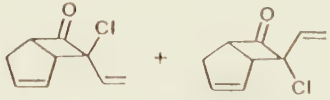
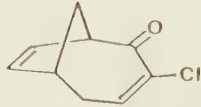
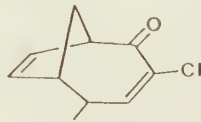
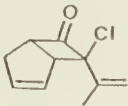
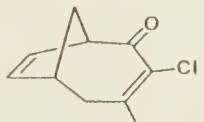
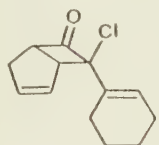
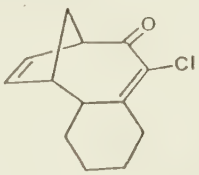
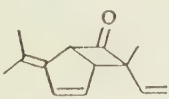
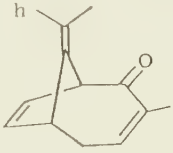
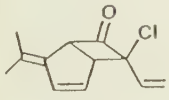
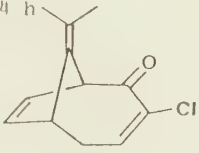
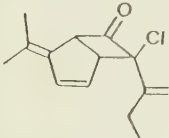
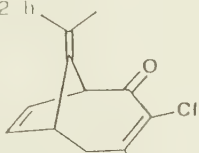
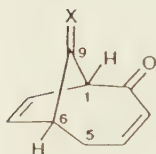
Cycloadducts	Rearrangement products
ratio	yield
rearrangement conditions	
 13a + 14a 3:7	160° neat, 1 h  17a 83%
 13e	150° xylene, 3 h  17e 90%
 13f + 14f 5:5	190° neat, 1 h  17f 48%
 13g + 14g 5:5	145° xylene, 12 h  17g 6%

Table 2 (continued):

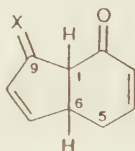
 <u>13h</u>	160° neat, 1 h  <u>17h</u> 81%
 <u>13j</u>	145° xylene, 4 h  <u>17j</u> 70%
 <u>15a</u>	145° xylene, 3 h  <u>18a</u> 54%
 <u>15f</u>	145° xylene, 4 h  <u>18f</u> 50%
 <u>15j</u>	145° xylene, 2 h  <u>18j</u> 45%

2.1. Structure of the thermal rearrangement products.

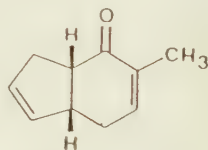
The following arguments support the structure of the rearrangement products 17 and 18 as shown in Scheme 3 and Table 2: From the UV.-maxima (230-265 nm) and the IR.-bands ($1660-1690\text{ cm}^{-1}$), both due to the conjugated enone system, it is evident that all nine products contain either the bicyclo[4.2.1]nonadienone (20) or the bicyclo[4.3.0]nonadienone skeleton (21), i.e. that they were formed by either a [3,3] or a [1,3] rearrangement of the cycloadducts 13-16.



20



21



22 a

Further evidence may be adduced first for the five rearrangement products 17, the series without the isopropylidene group. Their $^1\text{H-NMR}$ -spectra all contain four characteristic signals, namely two due to a CH_2 -group (near 1.8-2.3 ppm) and two due to two CH -groups (near 3.5-3.7 and 3.0-3.3 ppm). These four signals may be produced by $\text{H}_2\text{-C}(9)$, $\text{H-C}(1)$ and $\text{H-C}(6)$ in either 20 or 21 ($\text{X} = \text{H}, \text{H}$). An analysis of their coupling pattern in the 360 MHz $^1\text{H-NMR}$ -spectrum of 17a confirms the presence of a CH_2 -bridge attached on both sides to two bridgehead CH -groups, a system pre-

sent in 20 but not in 21 ($X = H, H$), as follows: 1) The geminal coupling of 12-13 Hz between the two $H-C(9)$'s is in better agreement with a non-allylic (as found in 20, $X = H, H$) than with an allylic CH_2 -group (as in 21, $X = H, H$). 2) One of the two $H-C(9)$'s shows almost equal coupling ($J = 6-7.5$ Hz), and the other no coupling, with two hydrogen atoms, a feature not expected for the substructure $-CH_2-CH-CH-$ in 21, but in good agreement with the substructure $-CH-CH_2-CH-$ in 20, $X = H, H$. 3) A coupling between $H-C(1)$ and $H-C(6)$, which would clearly be expected if these H -atoms were vicinal (cis or trans) neighbors as in 21, is not observed. Furthermore, a compound with the skeleton of 20, $X = H, H$, namely its 3-methyl-derivative 22a, was synthesized (see Section 3.2) in this work; its 360 MHz. 1H -NMR.-spectrum confirmed that the features discussed above (along with further ones) are indeed characteristic for the difference between 20 and 21 ($X = H, H$).

Concerning the three rearrangement products 18 with the isopropylidene group, their well separated 1H -NMR.-signals for $H-C(6)$ (4.30-3.96 ppm) and $H-C(1)$ (3.75-3.45 ppm) exhibit only very small or no couplings. This eliminates the skeleton 21 ($X = C(CH_3)_2$) and thus establishes 20 ($X = C(CH_3)_2$) for the rearrangement products 18.

2.2. Mechanism of the thermal rearrangement.

A simple [3s,3s]-sigmatropic rearrangement cannot be postulated for all the observed thermal transformations, since a pericyclic transition state from the vinyl-exo-isomers (14 and 16) would be energetically disfavored. Of interest in this connection would be the configuration at C(5) of 17 in the cases e, g and j; without the other diastereoisomer being available, it is difficult to draw a conclusion at present on the concertedness of the observed rearrangement.

3. Acid-catalyzed rearrangements of the vinylketene/cyclopentadiene-adducts

3.1. Reactions and products

The vinylketene/cyclopentadiene adducts 13a/14a, 13b/14b, 13c, 13d/14d, 13e and 13j were subjected to reaction under acid catalysis. For 13a/14a and 13b/14b, neat BF_3 -etherate was chosen because the reaction was too slow in diluted solutions; with CF_3COOH , complex mixtures resulted. For the rearrangements of 13c and 13d/14d, BF_3 -etherate diluted with dimethoxyethane sufficed; in other solvents more by-products were formed. The cycloadducts 13e and 13j were rearranged under the influence of both BF_3 -etherate and CF_3COOH , yielding, in each case, the same product. Starting materials, conditions and results of these reactions are shown in Table 3.

From the treatment of the cycloadducts 13a/14a and 13b/14b, with BF_3 -etherate the bicyclo[4.3.0]nonadienones 22a and 22b were isolated in moderate yields. Gas chromatographic examination of the crude rearrangement products showed, that in both cases, some of the corresponding bicyclo[4.2.1]nonadienones 17a and 17b [58] were also formed. The spectra of 22a and 22b showed them to contain a conjugated α -methyl-enone system (UV.: 236nm / ϵ = 6500-8000, IR.: 1668-1670 cm^{-1} and $^1\text{H-NMR}$.: 1.75-1.78 ppm), which could either correspond to a bicyclo[4.3.0]- (21a) or a bicyclo[4.2.1]nonadienone-skeleton (20a). The latter was excluded by three $^1\text{H-NMR}$ -signals (360 MHz) in both 22a and 22b, namely one

Table 3: Summary of results on the acid-catalyzed rearrangement of
vinylketene/cyclopentadiene adducts (13/14)

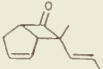
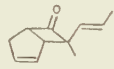
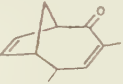
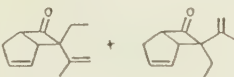
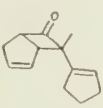
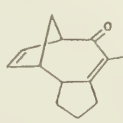
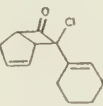
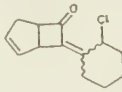
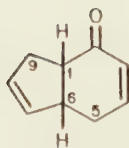
Cycloadducts ratio	conditions	observed products ratio(s) ¹⁾	isolated product(s) yield(s)
 +  <u>13a</u> <u>14a</u> 3:7	BF ₃ -etherate	 <u>22a</u> 80	 <u>17a</u> 20 (51%)
 +  <u>13b</u> <u>14b</u> 40:60 98:2 2:98	BF ₃ -etherate BF ₃ -etherate BF ₃ -etherate	 <u>22b1+22b2</u> (28+49) (21+37) (30+60)	 <u>17b</u> 23 42 10 (54%)
 <u>13c</u>	BF ₃ -etherate in DME in CH ₃ CN in CH ₂ Cl ₂ in CHCl ₃ in CCl ₄ in diethylether in diisopropylether in diglyme	 <u>23c</u> 80 0 24 22 20 69 29 76	 <u>17c</u> 20 100 76 78 80 31 71 24 (36%) (10%)

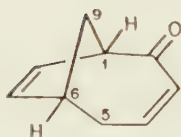
Table 3 (continued):

 <u>13d</u> <u>14d</u> 10:1	 <u>23d</u> <u>17d</u> 80 : 20 BF₃-etherate in DME	<u>23d</u> <u>17d</u> (35%) (7%)
 <u>13e</u>	 <u>17e</u> a) BF₃-etherate b) CF₃COOH	<u>17e</u> (45%) (62%)
 <u>13j</u>	 <u>24j</u> a) BF₃-etherate b) CF₃COOH	<u>24j</u> (50%) (91%)

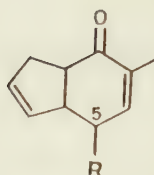
¹⁾ Observed in the crude rearrangement product by gas chromatography



21a



20a

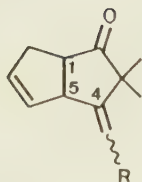


22 a: R = H

22 b: R = CH₃

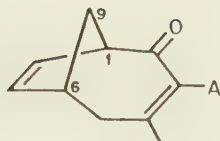
for a methylene-group (2.55-2.7 ppm), which does not correspond to a non-allylic position (H₂-C(9) in 20a), and two for methine-protons (2.87-2.94 and 2.86-3.28 ppm) with a mutual coupling of 7.6-8 Hz, which excludes their non-vicinal position (H-C(1) and H-C(6) in 20a) (cf. Section D.2.1). The latter coupling establishes the (expected) cis-ring fusion in 22a and 22b. The 5-methyl-derivative 22b consisted of a 6:4 mixture of two diastereoisomers 22b1 and 22b2; although they were separated from each other, it has so far not been possible to determine their configuration at C(5).

From the treatment of the cycloadducts 13c and 13d/14d with BF₃-etherate in dimethoxyethane the 4-alkylidenebicyclo-[3.3.0]octenones 23c and 23d were isolated in moderate yields, accompanied, in both cases, by lesser amounts of the bicyclo[4.2.1]nonadienones 17c and 17d. The properties of 17c and 17d clearly showed them to possess the skeleton 20a, which has been discussed in Section D.2.1. With respect to 23c and 23d, their UV. (no maxima in the range of 220-240 nm) and IR. (1743 cm⁻¹) spectra characterize them as five-membered ring ketones without conjugation.



23c: R=H

23d: R=CH₃

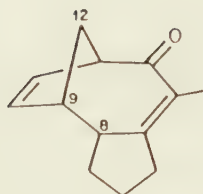


17c: A=CH₃

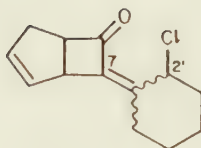
17d: A=CH₂CH₃

Their ¹H-NMR.-signals for two vinyl H (in 23c) or for one vinyl H (in 23d) points to an exocyclic double bond and the signals for a doubly allylic proton ($\delta = 4.00$ and 4.14 ppm) and for two diastereotopic geminal methyl groups confirm structure 23. The coupling constant of 8 Hz between H-C(1) and H-C(5) indicates a cis ring fusion between the two five-membered ring. In the case of 23c, the ratio of 23c to 17c was found to be solvent dependent. Using eight solvents (see Table 3), the two extremes were 100% of 17c in acetonitrile and an 8:2 ratio of 23c:17c in dimethoxyethane or diglyme.. This solvent effect does not appear to correlate either with the polarity or the dielectric constant of the solvent.

When the cycloadduct 13e was exposed either to BF₃-etherate or to CF₃COOH only the bicyclo[4.2.1]nonadienone 17e was observed, as a single diastereoisomer which was identical to that obtained from the thermal rearrangement of 13e (see Section D.2).



17e



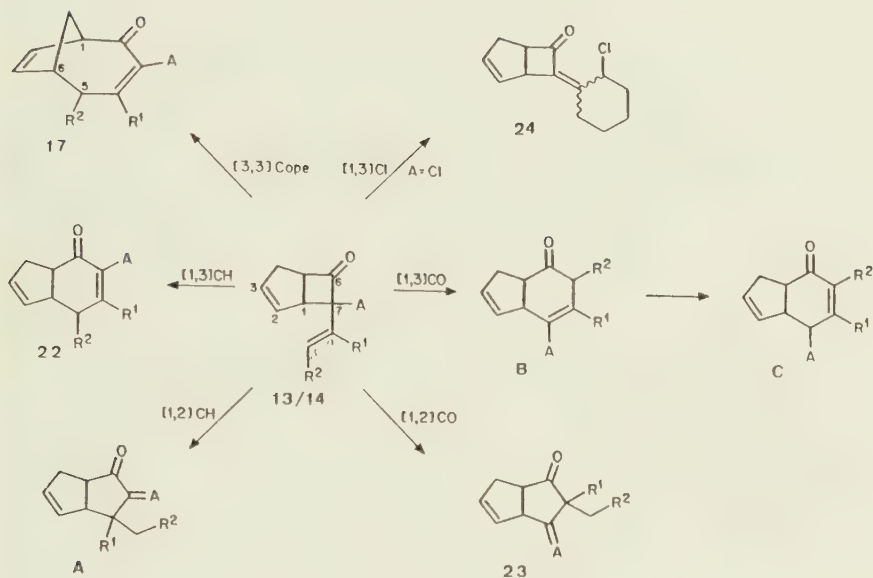
24j

The rearrangement of 13j in presence of both BF_3 -etherate and CF_3COOH proceeded without rearrangement of the carbon skeleton to yield the 7-alkylidenebicyclo[3.2.0]heptenone 24j. The product was only one of the four possible diastereoisomers. The spectral features of known [16][19] 7-alkylidenebicyclo[3.2.0]heptenones without a chlorine atom are similar to those of 24j (UV.: 249/10600, IR.: 1750 and 1670 cm^{-1} and $^1\text{H-NMR}$.-signals for H-C(1) and H-C(5) near 4.2-3.4 ppm). The configuration of the Cl-atom and the double bond in 24j could not be determined.

3.3. Reaction paths of the acid-catalyzed rearrangements

The vinylketene/cyclopentadiene adducts 13/14 contain the following functional moieties potentially sensitive to acid catalysis: an α -vinylcyclobutanone, two allylic, one Cope and (in the case of 13j) an allyl chloride system(s). The isolated products show that, of the numerous rearrangements conceivable for 13/14 under these circumstances, the following four actually occurred (abbreviation for rearrangement: transformation of bonds i,j $\rightarrow$ k,l): [3,3] Cope: 1,7 $\rightarrow$ 3,3, [1,3]CH: 1,7 $\rightarrow$ 1,3, [1,2]CO: 6,7 $\rightarrow$

Scheme 4

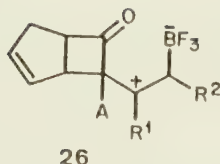
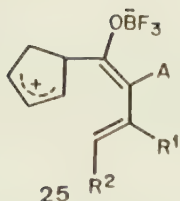


6, α , and [1,3]Cl: 7, A $\longrightarrow$ 3, A. Scheme 4 shows the observed rearrangements (four) together with (two) conceivable ones, which had to be considered as reasonable alternatives. (The products which were not observed are designated with letters).

The following arguments show that A, B (and C) are not among the isolated products: None of the products contained a conjugated enone together with an exocyclic double bond, which would be expected for the bicyclo[3.3.0]system A, and none of them a non-conjugated cyclohexenone, as expected for B, which would most likely be converted to C during the isolation. While C is not distinguishable from 22 for the example 22b with $A = R^2 = CH_3$, $R^1 = H$, the other example 22a with $A = CH_3$, $R^2 = R^1 = H$, however, excludes C by the absence of 1H -NMR. signals for two vicinal enone protons and for a methyl group attached to CH.

The [1,3]Cl rearrangement appears to be strongly preferred over other reactions when $A = Cl$. The driving force for this allylic chloride rearrangement 13j $\longrightarrow$ 24j must be the migration of the double bond into conjugation. The functionalities in and the ready availability of 24 may confer some synthetic interest to compounds of this type.

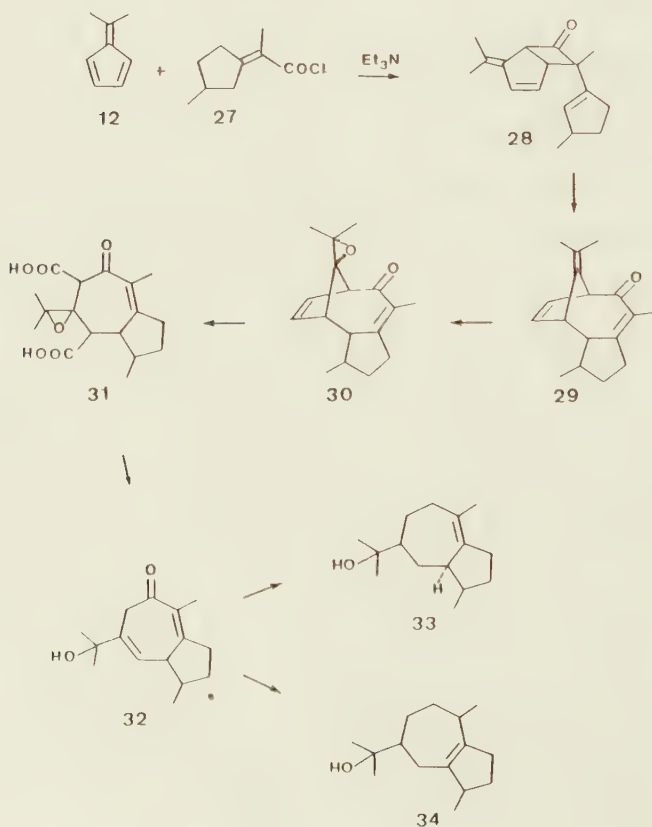
The driving force for the three carbon skeleton rearrangements is probably the strain relief due to the expansion of the four-membered ring. The difference in activation energy between the [1,3]CH, the [1,2]CO and the [3,3] Cope rearrangement under acid catalysis in this system must be small, since relatively minor variations of R^1 and R^2 already cause a change of reaction preference. For this reason a working hypothesis cannot be proposed, at present, for further experiments. It appears likely that a species with the boron-atom complexed on the oxygen-atom (such as 25) is involved in the [1,3]CH rearrangement, whereas a species with the boron-atom complexed at C(β) (such as 26) may be passed



through in the [1,2]CO rearrangement. The [3,3] Cope rearrangement, which occurs thermally (see Section D.2), is evidently also catalyzed by acids (BF_3 , TiCl_4 and CF_3COOH). A possible difference in the behavior of the two C(7)-stereoisomers, the vinyl-endo- (13) and the vinyl-exo- (14) isomers, was investigated in the case of 13b/14b by determining the component distribution in the crude rearrangement product by gas chromatography. Thus the ratio 22b:17b using pure 13b and pure 14b was 60:40 and 90:10, respectively. Two diastereomeric transition states are available for each reaction type, one with the C(α),C(β) double bond pointing over and the other away from the four-membered ring. While the configuration of the side chain double bond of 13b, 14b and 13e could be derived, it was not possible to establish the configuration of the rearrangement products 22b at C(5) and 17e at C(8). Thus no information is available on the nature of the transition states. The migration of C(1) in the [1,3]CH rearrangement occurred with retention of configuration.

4. A Proposal for the synthesis of two terpenoid natural products
using the cycloaddition of a vinylketene

Of the numerous naturally occurring sesquiterpenes, guaiol and bulnesol have been selected here to demonstrate a possible application of one the reactions studied in this work. Bulnesol (33) and guaiol (34) are hydroazulenic sesquiterpenes consisting of a five and seven membered ring. A short synthetic scheme is pro-



posed below which includes, as key reactions, the [2+2] cycloaddition of a vinylketene to 6,6-dimethylfulvene and the [3,3] rearrangement of the resulting cycloadduct.

The acid chloride 27 might be used for a cycloaddition of the derived vinylketene to 6,6-dimethylfulvene 12 at temperatures above 80°, conditions which could furnish the tricyclic ketone 29 directly, via a [3,3] Cope rearrangement of 28. Selective epoxidation of the latter to 30, followed by oxidative cleavage of the isolated double bond might provide the desired hydroazulenenic skeletons 31 and from it, by means of two β -assisted decarboxylations, the hydroxyketone 32, which could be modified to either +bulnesol (33) or +guaiol (34).

Some preliminary experiments have been carried out and show promising results. Using the rearrangement product 18a (see Section D.2, p. 47) as a model system, the validity of the proposed reaction sequence was tested [59]. The latter study can already be said to provide an easy entry into selectively functionalized seven-membered ring systems.

E. Experimental Part

1. General.

1.1. Chromatographic methods.

TLC.-A = Thick layer chromatography on plates coated with silica-gel 60 F₂₅₄ Merck, 20 x 20 cm, thickness 2 mm. Detection: UV lamp. Description: (TLC.-A, eluent, R_f value). LC.-A = Column chromatography on Merck "Lobar" columns filled with silicagel LiChroprep Si20 (40-63 u) at 2-6 bar pressure. GC.-A = gas chromatography on WCOT columns (12-25 m x 0.2-0.3 mm) with H₂ as carrier gas, FI-detector. GC.-B = Semipreparative gas chromatography on packed glass columns, 1-4 m x 4 mm iD, 5-10% stationary phase on chromosorb W/AW-DMCS, 80/100 mesh, carrier gas He, TC-detector.

1.2. Melting points (mp.)

Melting points were determined on a Mettler FP 52 apparatus with a microscope and are corrected.

1.3. Spectroscopy

1.3.1. Ultraviolet spectra (UV.)

Recorded on a Perkin Elmer 555 or a Uvikon 810 instrument.

Description: UV. (solvent): wavelength of the maxima in nm/
molar extinction.

1.3.2. Infrared spectra (IR.)

Recorded on a Perkin Elmer instrument. Description: IR. (medium):
wavenumber in cm^{-1} with intensity, (interpretation). Notations
used: s=strong, m=medium, w=weak and br=broad.

1.3.3. Proton magnetic resonance spectra (^1H -NMR.)

Recorded with the following instruments: Varian EM-360 (60 MHz),
Varian EM-390 (90 MHz), Varian FT-80 (80 MHz), Varian XL-200 (200
MHz), Bruker HX-360 (360 MHz) and Bruker WH-400 (400 MHz).

Description: ^1H -NMR. (frequency, solvent): δ value in ppm/mul-
tiplicity (coupling constants in Hz, number of protons,
interpretation). Notations: s=singlet, d=doublet, t=triplet,
qa=quartet, qi=quintet, m=multiplet and br.=broad. Tetramethylsi-
lane was used as internal standard ($\delta=0$ ppm). For ^1H -NMR. decou-
pling experiments the chemical shift of the irradiated signal is
given in square brackets [δ], followed by the multiplicity of the
ensuing signal.

1.3.4. ^{13}C -magnetic resonance spectra (^{13}C -NMR.)

Recorded on a Varian XL-200 (50 MHz) or Varian FT-80 (20 MHz) spectrometer. Description: ^{13}C -NMR.(solvent): δ value in ppm/multiplicity (interpretation). Notations: s=singlet, d=doublet t=triplet and q=quartet. Tetramethylsilane was used as internal standard ($\delta=0$ ppm).

1.3.5. Mass spectra (MS.)

Measured on Varian MAT 711 and CEC 21-110B spectrometers.

Description: MS. (molecular weight): mass of the ion/intensity (interpretation when possible). Only peaks above 10% intensity of the base peak are given.

1.4. Purities

The purity of all substances were checked by gas-liquid chromatography and elemental analysis.

1.5. Acknowledgements

The elemental analyses were performed by the Micro laboratory (Mr. H. Frohofer and his staff). The 200-MHz, 90-MHz and the ^{13}C -NMR. spectra were measured in the NMR. laboratory under the direction of Prof. von Philipsborn. The 360 and 400 MHz spectra were measured by Spectrospin AG in Fällanden. The mass spectra were obtained from the mass spectrometry laboratory under the direction of Prof. M. Hesse.

2. Preparation of α -alkyl- and α -chloro- α,β -unsaturated acids.

2.1. General procedure.

To a stirred suspension of 110-120 mmol NaH (55-60% dispersion in mineral oil) in 150 ml dry dimethoxyethane was added 105 mmol of triethyl 2-phosphonopropionate (2), triethyl 2-phosphonobutyrate (3) [46] or triethyl 2-chloro-2-phosphonoacetate (4) [47], during 20 min at 0°. The mixture was stirred at RT. for 30 min, treated with 100 mmol of the carbonyl compound (1) at once, refluxed for 1 to 6 h, cooled, diluted with water and extracted with ether. The combined ethereal extracts were dried over Na₂SO₄ and evaporated. The residual ester (5) was heated for 15 h in a refluxing mixture of 200 mmol of NaOH, 40 ml of water and 30 ml of ethanol. After cooling and removing the ethanol, the mixture was washed twice with ether, the aqueous phase acidified with 10% hydrochloric acid and extracted three times with ether. The combined ethereal extracts were dried (Na₂SO₄), concentrated and the residual acid (6) was either distilled in a Kugelrohr or recrystallized.

2.2. (E)-2-Methyl-2-pentenoic acid (6b).

From 7.8 ml (105 mmol) propionaldehyde and 25 g (105 mmol) triethyl 2-phosphonopropionate (2), after recrystallization from hexane at 0°, was obtained 8.0 g (67%) 6b, mp. 15-20° ([48]: bp. 123-125°/30 Torr).- ¹H-NMR. (60 MHz, CDCl₃): 11.76/s (1 H, OH); 6.93/br. t (J = 7, 1 H, H-C(3)); 2.23/qi (J = 7, 2H, 2H-C(4)); 1.83/s (3H, CH₃-C(2)); 1.07/t (J = 7, 3H, CH₃-C(4)).

2.3. 2,3-Dimethyl-2-butenic acid (6c).

From 7 ml (95 mmol) acetone and 24 g (101 mmol) triethyl 2-phosphonopropionate (2), after recrystallization from pentane, was obtained 9.5 g (88%) 6c as colorless needles, mp. 69-70° ([49]: mp. 68-68.5°).- ¹H-NMR. (60 MHz, CDCl₃): 11.64/s (1 H, OH); 2.10/s, 3 H and 1.86/s, 6H (together 9H, CH₃-C(2), 2CH₃-C(3)).

2.4. 2-Ethyl-3-methyl-2- (6d) and 2-ethyl-3-methyl-3-butenic acid (9).

From 9.1 ml (100 mmol) acetone and 33 g (131 mmol) triethyl 2-phosphonobutyrate (3), after distillation at 140-150°/12 Torr, was obtained 11.0 g (70%) of a yellow oil consisting of a 55:45 mixture of 6d ([50]: mp. 47-48°) and 9, respectively.- ¹H-NMR. (60 MHz, CDCl₃): 10.80/s (2H, OH of 6d and OH of 9); 5.00/split s (2H, 2H-C(4) of 9); 3.00/t (J = 7, 1 H, H-C(2) of 9); 2.20/qa (J = 7, 2H, 2H-C(1') of 6d); 2.12/s and 1.92/s (6H, 2CH₃-C(3) of

6d); 2.0-1.57/m (2H, 2H-C(1')) of 9); 1.82/split s (3H, CH₃-C(3) of 9); 0.91/t and 1.02/t (both J=7, 6H, CH₃-C(1') of 6d and CH₃-C(1') of 9).

2.5. 2-Cyclopentylidenepropionic acid (6e).

From 8.9 ml (100 mmol) cyclopentanone and 24.6 g (103 mmol) triethyl 2-phosphonopropionate (2), after crystallization from pentane, was obtained 6.9 g (49%) 6e as colorless needles, mp.

106-108°.- IR. (CHCl₃): 1670s (C=O), 1620m (C=C).- ¹H-NMR. (90 MHz, CDCl₃): 11.0/s (1 H, OH); 2.93-2.63/m and 2.46-2.23/m (each 2H, 2H-C(2') and 2H-C(5')); 1.86/split s (3H, CH₃-C(2)); 1.8-1.56/m (4H, 2H-C(3') and 2H-C(4')).

C₈H₁₂O₂ (140.18) Calc. C 68.54 H 8.63% Found C 68.40 H 8.54%

2.6. (Z)-2-Chloro-2-butenic acid (6f).

From 2.2 ml (39 mmol) acetaldehyde and 10.3 g (40 mmol) triethyl 2-chloro 2-phosphonopropionate (4), after recrystallization from hexane, 3.39 g (72%) of (Z)-6f was obtained as colorless crystals, mp. 98.5° ([51]: mp. 99.5°).- ¹H-NMR. (60 MHz, CDCl₃): 9.45/s, (1 H, OH); 7.31/qa (J = 7, 1 H, H-C(3)); 1.98/d (J = 7, 3H, CH₃).

2.7. 2-Chloro-2-pentenoic acid (6g).

From 4.3 ml (59 mmol) propionaldehyde and 16 g (62 mmol) of triethyl 2-chloro-2-phosphonoacetate, after distillation at 120°/12 Torr, 4.32 g (54%) of a 7:3 mixture of (Z)- and (E)-6g was obtained as a colorless oil ([52]: mp. 48.5-49.5° for the (Z)-acid).- ¹H-NMR. (60 MHz, CCl₄): 11.70/s (1 H, OH); 7.16/t and 6.54/t (both J = 7, together 1 H, H-C(3)); 2.40/qi and 2.63/qi (both J = 7, together 2H, 2H-C(4)); 1.15/t and 1.13/t (both J = 7, together 3H, CH₃-C(4)).

2.8. 2-Chloro-3-methyl-2-butenic acid (6h).

From 4.3 ml (58 mmol) acetone and 15.5 g (60 mmol) of triethyl 2-chloro-2-phosphonoacetate (4), after recrystallization from hexane, 3.4 g (43%) 6h was obtained as pale-yellow crystals, mp. 85-87° ([53]: mp. 85-86°).- ¹H-NMR. (60 MHz, CDCl₃): 10.80/s (1 H, OH); 2.23/s and 2.06/s (each 3H, 2CH₃-C(3)).

2.9. 2-Chloro-3-methyl-2-pentenoic acid (6i).

From 13.4 ml (150 mmol) ethylmethylketone and 40 g (155 mmol) of triethyl 2-chloro-2-phosphonoacetate (4), after distillation at 140-150°/12 Torr, 11.3 g (51%) of a mixture consisting of (Z)- and (E)-6i was obtained in a 1:1 ratio and about 10% of what might be the β,γ-unsaturated isomer of 6i ([54]: bp. 73-76°/0.05 Torr) as a pale-yellow oil.- ¹H-NMR. (60 MHz, CDCl₃): 10.86/s (1 H, OH); 2.65/qa and 2.45/qa (both J = 7, together 2H, 2H-C(4));

2.23/s and 2.05/s (together 3H, CH₃-C(3)); 1.10/t (J = 7, 3H, CH₃-C(4)). The β,γ -unsaturated isomer manifested itself by the signals of its vinyl protons.

2.10. 2-Chloro-2-cyclohexylideneacetic acid (6j)

From 7.1 ml (69 mmol) cyclohexanone and 18.6 g (72 mmol) of triethyl 2-chloro-2-phosphonoacetate (4), after recrystallization from hexane, 7.7 g (64%) 6j was obtained as colorless crystals, mp. 100-101° ([55]: mp. 101-102°).- ¹H-NMR. (60 MHz, CDCl₃): 11.75/s (1 H, OH); 2.96-2.34/m (4 H, 2H-C(2') and 2H-C(6')); 1.66/br. s (6H, 2H-C(3'), 2H-C(4') and 2H-C(5')).

3. Preparation of α -alkyl- and α -chloro- α,β -unsaturated acid chlorides (7).

3.1. General procedure.

A mixture of 1 mequiv. α -alkyl- and α -chloro- α,β -unsaturated acid (6) and 2 mequiv. thionyl chloride was refluxed for 4 h, cooled, the excess thionyl chloride removed and the residue distilled at reduced pressure in a Kugelrohr. The α,β -unsaturated acid chlorides (7) prepared in this way were pure by their ¹H-NMR.-spectra.

3.2. (E)-2-Methyl-2-pentenoyl chloride (7b).

From 8.0 g (70 mmol) (E)-2-methyl-2-pentenoic acid (6b) and 16.7 g (140 mmol) thionyl chloride was obtained 8.1 g (87%) of 7b as a colorless liquid, bp. 90-100°/12 Torr.- ¹H-NMR. (60 MHz, CDCl₃): 7.19/split t (J = 7, 1 H, H-C(3)); 2.32/split qi (J = 7, 2H, 2H-C(4)); 1.92/split s (3H, CH₃-C(2)); 1.12/t (J = 7, 3H, CH₃-C(3)).

3.3. 2,3-Dimethyl-2-butenoyl chloride (7c).

From 9.5 g (83 mmol) 2,3-dimethyl-2-butenic acid (6c) and 19.5 g (164 mmol) thionyl chloride was obtained 7.3 g (66%) 7c as a colorless liquid, bp. 80-100°/12Torr.- ¹H-NMR. (60 MHz, CDCl₃): 2.06/s, 6H and 1.92/s, 3H (together 9H, 2CH₃-C(3) and CH₃-C(2)).

3.4. 2-Ethyl-3-methyl-2- (7d) and 2-ethyl-3-methyl-3-butenoyl chloride (10).

From 11.0 g (86 mmol) of the 55:45 mixture of 2-ethyl-3-methyl-2- (6d) and 2-ethyl-3-methyl-3-butenic acid (9) and 20.5 g (172 mmol) thionyl chloride was obtained 10.4 g (83%) of a 1:1 mixture (¹H-NMR.) of 7d and 10 as a colorless liquid, bp. 90-100°/12 Torr.- ¹H-NMR. (60 MHz, CDCl₃): 5.08/t (J = 2, 1 H, H-C(4) of 10); 5.00/br. s (1 H, H-C(4) of 10); 3.30/t (J = 7, 1 H, H-C(2) of 10); 2.50/qa (J = 7, 2H, 2H-C(1') of 7d); 1.96/s and 1.90/s (6H, 2CH₃-C(3) of 7d); 1.76/split s (3H, 2CH₃-C(3) of 10); 2.12-1.60/m (2H, 2H-C(1') of 10); 1.10/t and 0.93/t (both J = 7, each 3H, CH₃-C(1') of 7d and CH₃-C(1') of 10).

3.5. 2-Cyclopentylidenepropionyl chloride (7e).

From 5.8 g (41 mmol) 2-cyclopentylidenepropionic acid (6e) and 9.8 g (82 mmol) thionyl chloride was obtained 5.5 g (84%) of 7e as a pale-yellow oil, bp. 70-80°/0.01 Torr.- ¹H-NMR. (90 MHz, CDCl₃): 2.83-2.30/m (4H, 2H-C(2') and 2H-C(5')); 2.03/split s (3H, CH₃-C(2)); 1.96-1.60/m (4H, 2H-C(3') and 2H-C(4')).

3.6. (Z)-2-Chloro-2-butenoyl chloride (7f).

From 8.0 g (66 mmol) (Z)-2-chloro-2-butenic acid (6f) and 15.7 g (132 mmol) thionyl chloride was obtained 5.7 g (62%) (Z)-7f as a colorless liquid, distilled at 70-100°/12 Torr.- ¹H-NMR. (60 MHz, CCl₄): 7.37/qa (J = 7, 1 H, H-C(3)); 1.9/d (J = 7, 3H, CH₃-C(3)).

3.7. 2-Chloro-2-pentenoyl chloride (7g).

From 2.44 g (18 mmol) 2-chloro-2-pentenoic acid (6g) and 4.3 g (36 mmol) thionyl chloride was obtained 1.6 g (57%) of an 8:2 mixture of (Z)- and (E)-7g as a colorless oil, distilled at 85°/12 Torr.- ¹H-NMR. (60 MHz, CCl₄): 7.46/t and 6.49/t (both J = 7, together 1 H, H-C(3)); 2.48/q1 (J = 7, 2H, 2H-C(4)); 1.18/t and 1.06/t (both J = 7, together 3H, CH₃-C(4)).

3.8. 2-Chloro-3-methyl-2-butenoyl chloride (7h).

From 3.1 g (23 mmol) 2-chloro-3-methyl-2-butenic acid (6h) and 5.9 g (50 mmol) thionyl chloride was obtained 2.43 g (69%) 7h as a pale-yellow oil, distilled at 100°/25 Torr.- ¹H-NMR. (60 MHz, CDCl₃): 2.1/s and 2.15/s (each 3H, 2CH₃-C(2)).

3.9. 2-Chloro-3-methyl-2-pentenoyl chloride (7i).

From 11.2 g (75 mmol) 2-chloro-3-methyl-2-pentenoic acid (6i) and 17.8 g (150 mmol) thionyl chloride was obtained 7.4 g (59%) of a 6:4 mixture of (Z)- and (E)-7i as a colorless oil, distilled at 95°/12 Torr.- ¹H-NMR. (60 MHz, CCl₄): 2.46/qa (J = 7, 2H, 2H-C(4)); 2.12/s and 2.05/s (together 3H, CH₃-C(3)); 1.13/t (J = 7, 3H, CH₃-C(4)).

3.10. 2-Chloro-2-cyclohexylideneacetyl chloride (7j).

From 3.5 g (20 mmol) 2-chloro-2-cyclohexylideneacetic acid (6j) and 4.8 g (40 mmol) thionyl chloride was obtained 3.5 g (90%) 7j as a colorless oil, distilled at 70-80°/0.03 Torr.- ¹H-NMR. (60 MHz, CCl₄): 2.53/br. s (4H, 2H-C(2') and 2H-C(6')); 1.68/br. s (6H, 2H-C(3'), 2H-C(4') and 2H-C(5')).

4. Preparation of the ketene-adducts (13/14 and 15/16).

4.1. General procedure.

To a stirred solution of 1 mequiv. α,β -unsaturated acid chloride (7) and 3-6 mequiv. of cyclopentadiene (11) or 1-2 mequiv. of 6,6-dimethylfulvene (12) in dry methylene chloride or ethanol-free chloroform was added slowly a solution of 1.05 mequiv. of triethylamine in the same solvent. After stirring for 15-48 h at RT., the mixture was washed three times with water, dried (Na_2SO_4) and concentrated. The residual ketene-adduct 13/14 or 15/16 was distilled at reduced pressure in a Kugelrohr and/or purified by chromatography.

4.2. 7-endo-Methyl-7-exo-(E)-propenyl- (14b) and 7-exo-methyl-7-endo-(E)-propenylbicyclo[3.2.0]- hept-2-en-6-one (13b)

From 4.0 g (30 mmol) 2-methyl-2-pentenoyl chloride (7b), 12 ml (110 mmol) cyclopentadiene (11) and 3.2 g (31.5 mmol) triethylamine in 30 ml CH_2Cl_2 was obtained 3.1 g of a crude oil, 1.0 g of which was chromatographed (LC.-A, hexane/ethyl acetate 97:3) to give 0.52 g (33%) of a 6:4 mixture of 14b and 13b. The two stereoisomers 14b and 13b were separated in this order by chromatography (LC.-A, hexane/ethyl acetate 95:5).

Data of 14b (98% pure, GC.-A, SE-52, 88°).- IR. (CCl_4): 1788s (C=O).- $^1\text{H-NMR}$. (200 MHz, CDCl_3): 5.94-5.84/m and 5.82-5.72/m

(each 1 H, H-C(2) and H-C(3)); 5.65-5.45/m (2H, H-C(1') and H-C(2')); 3.96/d x d x d ($J = 9, 7.5$ and 2 , 1 H, H-C(5)); 3.48-3.36/m (1 H, H-C(1)); 2.66/d x qi ($J = 17$ and 2 , 1 H, H_{endo}-C(4)); 2.40/d x d x qa ($J = 17, 9$ and 2 , 1 H, H_{exo}-C(4)); 1.60/d x d ($J = 6$ and 1.5 , 3H, CH₃-C(2')); 1.06/s (3H, CH₃-C(7)). The olefinic protons H-C(1') and H-C(2') were shifted by the addition of Eu(fod)₃ to give a splitting pattern at 6.42/br. d ($J = 15.5$, 1 H, H-C(1')) and 6.60/ d x qa ($J = 15.5$ and 6 , 1 H, H-C(2')).
¹H-NMR. (200 MHz, C₆D₆): 5.6-5.3/m (4H, H-C(2), H-C(3), H-C(1') and H-C(2')); 3.58/d x d x d ($J = 9, 7.5$ and 1.5 , 1 H, H-C(5)); 3.10-3.00/m (1 H, H-C(1)); 2.59/br. d ($J = 17$, 1 H, H_{endo}-C(4)); 2.02/d x d x qa ($J = 17, 9$ and 2 , 1 H, H_{exo}-C(4)); 1.50/d ($J = 5$, 3H, CH₃-C(2')); 1.05/s (3H, CH₃-C(7)).

C₁₁H₁₄O (162.23) Calc. C 81.44 H 8.70% Found C 81.08 H 8.98%

Data of 13b (99% pure GC.-A, SE-52, 88°).- IR (CCl₄): 1787s (C=O).- ¹H-NMR. (200 MHz, CDCl₃): 5.94-5.84/m and 5.80-5.70/m (each 1 H, H-C(2) and H-C(3)); 5.60/d x qa ($J = 15.5$ and 6 , 1 H, H-C(2')); 5.50/d x qa ($J = 15.5$ and 1.5 , 1 H, H-C(1')); 3.96/d x d x d ($J = 9, 7.5$ and 2 , 1 H, H-C(5)); 3.36-3.22/m (1 H, H-C(1)); 2.68/d x qi ($J = 17$ and 2 , 1 H, H_{endo}-C(4)); 2.45/d x d x qa ($J = 17, 9$ and 2 , 1 H, H_{exo}-C(4)); 1.68/d x d ($J = 6$ and 1.5 , 3H, CH₃-C(2')); 1.41/s (3H, CH₃-C(7)).- ¹H-NMR. (200 MHz, C₆D₆): 5.61/d x qa ($J = 15.5$ and 6.5 , 1 H, H-C(2')); 5.58-5.47/m (2H, H-C(2) and H-C(3)); 5.36/d x qa ($J = 15.5$ and 1.5 , 1 H, H-C(1')); 3.45/d x d x d ($J = 9, 7.5$ and 2 , 1 H, H-C(5)); 2.87-2.76/m (1 H, H-C(1)); 2.57/d x m ($J = 17$, 1 H, H_{endo}-C(4)); 2.09/d x d x qa ($J = 17, 9$ and 1.5 , 1 H, H_{exo}-C(4)); 1.54/d x d ($J = 6.5$ and 1.5 ,

3H, CH₃-C(2'))); 1.16/s (3H, CH₃-C(7)).- MS. (162): 162/6 (M); 134/18; 96/100; 91/37; 66/18; 41/51.

C₁₁H₁₄O (162.23) Calc. C 81.44 H 8.70%, Found C 81.31 H 8.70%.

4.3. 7-endo-Isopropenyl-7-exo-methylbicyclo[3.2.0]hept-2-en-6-one (13c).

From 7.2 g (54 mmol) 2,3-dimethyl-2-butenoyl chloride (7c), 30 ml (364 mmol) cyclopentadiene (11) and 5.6 g (55 mmol) triethylamine in 50 ml CHCl₃ was obtained, after 26 h reaction time, 4.6 g of a crude oil, which was separated into two components by chro-

matography (LC.-A, hexane/ether 9:1) to yield 1.8 g (28%) of 13c and 0.8 g (12%) of 3,4-dimethylbicyclo[4.2.1]nona-3,7-dien-2-one (17c), both as colorless oils.

Data of 13c.- IR. (CCl₄): 1775s (C=O).- ¹H-NMR. (60 MHz, CCl₄): 5.9-5.5/m (2H, H-C(2) and H-C(3)); 4.86/br. s (1 H, H-C(1')); 4.64/split s (1 H, H-C(1')); 3.76/d x d x d (J = 8, 8 and 2, 1 H, H-C(5)); 3.4-3.1/m (1 H, H-C(1)); 2.9-2.0/m (2H, 2H-C(4)); 1.67/br. s (3H, CH₃-C(2')); 1.40/s (3H, CH₃-C(7)).- ¹H-NMR. (200 MHz, C₆D₆): 5.58-5.45/m (2H, H-C(2) and H-C(3)); 5.26/qa x d (J = 1 and 1.5, 1 H, H-C(1')); 4.76/qa x d (J = 1.5 and 1.5, 1 H, H-C(1')); 3.38/d x d x d (J = 8.5, 7 and 1.5, 1 H, H-C(5)); 2.90-2.80/m (1 H, H-C(1)); 2.54/d x m (J = 17, 1 H, H_{endo}-C(4)); 2.08/d x d x qa (J = 17, 9 and 2, 1 H, H_{exo}-C(4)); 1.50/d x d (J = 1.5 and 1, 3H, CH₃-C(2')); 1.16/s (3H, CH₃-C(7)).- MS. (162): 162/13 (M); 147/10; 96/100; 68/46; 67/42; 66/9; 41/12 .

C₁₁H₁₄O (162.23) Calc. C 81.44 H 8.70% Found C 80.39% H 9.00%.

Data of 17c (99% pure, GC.-A, SE-52, 88°).- IR. (CCl₄): 1650 (C=O), 1605 (C=C).- ¹H-NMR. (200 MHz, CDCl₃): 6.00-5.84/m (2H, H-C(7) and H-C(8)); 3.54/d x d (J = 7 and 2.5, 1 H, H-C(1)); 3.06-2.95/m (1 H, H-C(6)); 2.85/br. d (J = 20, 1 H, H-C(5)); 2.52/br. d (J = 20, 1 H, H-C(5)); 2.13/d x d x d (J = 12.7, 7.7 and 7.7, 1 H, H_{anti}-C(9)); 1.96/d (J = 12.7, 1 H, H_{syn}-C(9)); 1.82/s and 1.80/s (each 3H, CH₃-C(3), CH₃-C(4)).- MS. (162): 162/14(M); 147/10; 96/100; 68/46; 67/38; 53/11; 41/14.

C₁₁H₁₄O (162.23) Calc. C 81.44 H 8.70% Found C 81.24 H 8.39%.

In another experiment the reaction mixture was stirred for 6 h under otherwise identical conditions to yield 20% of 13c and 4% of 17c. In refluxing benzene for 16 h, a 6:4 mixture of 13c and 17c was obtained, the yield of 13c was 10%.

4.4. 7-exo-Ethyl-7-endo-isopropenyl- (13d) and 7-endo-ethyl-7-exo-isopropenylbicyclo[3.2.0]hept-2-en-6-one (14d).

From 5.0 g (34 mmol) 2-ethyl-3-methyl-2- (7d) and 2-ethyl-3-methyl-3-butenoyl chloride (10) (6:4 mixture), 19 ml (230 mmol) cyclopentadiene(11) and 3.6 g (35 mmol) triethylamine in 40 ml CHCl₃ at RT. after 16 h was obtained, upon chromatography (LC.-A, pentane/ether 95:5), 0.63g (10%) of a 10:1 mixture of two stereoisomers 13d and 14d.- IR. (CCl₄): 1770s (C=O).- MS. (176): 176/10 (M); 110/100; 82/51; 66/24; 41/23.

C₁₂H₁₆O (176.26) Calc. C 81.77 H 9.15% Found C 81.63 H 9.40%.

The two compounds 13d and 14d of this mixture were separated by chromatography (LC.-A, hexane/ethyl acetate 95:5).

Data of 13d (95% pure, GC.-A, SE-52, 90°).- ¹H-NMR. (200 MHz, CDCl₃): 5.90-5.80/m and 5.74-5.64/m (each 1 H, H-C(2) and H-C(3)); 5.02/split s (1 H, H-C(1')); 4.88/split s (1 H, 1 H-C(1')); 3.83/d x d x d (J = 9, 7 and 2, 1 H, H-C(5)); 3.36-3.24/m (1 H, H-C(1)); 2.64/d x qi (J = 17 and 2, 1 H, H_{endo}-C(4)); 2.44/d x d x qa (J = 17, 9 and 2, 1 H, H_{exo}-C(4)); 1.95/d x qa (J = 14 and 7, 1 H, H-C(3')); 1.84/d x qa (J = 14 and 7, 1 H, H-C(3')); 1.64/split s (3H, CH₃-C(2')); 0.88/t (J = 7, 3H, CH₃-C(3')).- ¹H-NMR. (200 MHz, C₆D₆): 5.57-5.46/m (2H, H-C(2) and H-C(3)); 5.40/qi (J = 1, 1 H, H-C(1')); 4.91/qi (J = 1, 1 H, H-C(1')); 3.38/br. d x d (J = 8 and 8, 1 H, H-C(5)); 2.88-2.78/m (1 H, H-C(1)); 2.55/d x m (J = 17, 1 H, H_{endo}-C(4)); 2.08/d x d x qa (J = 17, 9 and 2, 1 H, H_{exo}-C(4)); 1.53/qa (J = 7, 2H, 2H-C(3')); 1.44/split s (3H, CH₃-C(2')); 0.87/t (J = 7, 3H, CH₃-C(3')). For elemental analysis, see mixture of 13d and 14d above.

Data of 14d (86% pure, GC.-A, SE-52, 90°).- ¹H-NMR. (200 MHz, CDCl₃): 5.98-5.85/m and 5.85-5.60/m (each 1 H, H-C(2) and H-C(3)); 5.01/split s (1 H, H-C(1')); 4.97/split s (1 H, H-C(1')); 3.86/d x d x d (J = 9, 8 and 2, 1 H, H-C(5)); 3.64-3.52/m (1 H, H-C(1)); 2.65/d x qi (J = 17 and 2, 1 H, H_{endo}-C(4)); 2.37/d x d x qa (J = 17, 9 and 2, 1 H, H_{exo}-C(4)); 1.76/split s (3H, CH₃-C(2')); 1.68/d x qa (J = 14 and 7, 1 H, H-C(3')); 1.46/d x qa (J = 14 and 7, 1 H, H-C(3')); 0.80/t (J =

7, 3H, $\text{CH}_3\text{-C}(3')$).- $^1\text{H-NMR}$. (200 MHz, C_6D_6): 5.63-5.56/m and 5.52-5.45/m (each 1 H, H-C(2) and H-C(3)); 4.99/br. s (1 H, H-C(1')); 4.89/qi (J = 1, 1 H, H-C(1')); 3.53/d x d x d (J = 9, 7 and 1.5, 1 H, H-C(5)); 3.30-3.20/m (1 H, H-C(1)); 2.56/d x m (J = 17, 1 H, $\text{H}_{\text{endo}}\text{-C}(4)$); 1.98/d x d x qa (J = 17, 8 and 2, 1 H, $\text{H}_{\text{exo}}\text{-C}(4)$); 1.68/d x qa (J = 14 and 7, 1 H, H-C(3')); 1.58/split s (3H, $\text{CH}_3\text{-C}(2')$); 1.36/d x qa (J = 14 and 7, 1 H, H-C(3')); 0.79/t (J = 7, 3H, $\text{CH}_3\text{-C}(3')$). For elemental analysis, see mixture of 13d and 14d above.

The yield of this cycloaddition did not improve when chloroform was used as solvent and when the reaction time was increased to 16 h and 26 h. When benzene was used as solvent and the reaction time prolonged to 48 h at RT. only 5% of 13d/14d was obtained.

4.5. 7-endo-Cyclopent-1'-enyl-7-exo-methylbicyclo[3.2.0]-hept-2-en-6-one (13e).

From 5.5 g (35 mmol) 2-cyclopentylidenepropionyl chloride (7e), 19 ml (230 mmol) cyclopentadiene (11) and 3.7 g (37 mmol) triethylamine in 30 ml CH_2Cl_2 was obtained after Kugelrohrdistillation at 120-130°/0.01 Torr, 4.8 g (74%) of 13e as a colorless oil (95% pure, GC.-A, SE-52, 107°).- IR. (CCl_4): 1780s (C=O).- $^1\text{H-NMR}$. (200 MHz, CDCl_3): 5.84-5.76/m and 5.65-5.57/m (each 1 H, H-C(2) and H-C(3)); 5.53/qi (J = 2, 1 H, H-C(2')); 3.88/d x d x d (J = 9, 7.5 and 2, 1 H, H-C(5)); 3.35-3.25/m (1 H, H-C(1)); 2.64/d x m (J = 17, 1 H, $\text{H}_{\text{endo}}\text{-C}(4)$); 2.43/d x d x qa (J = 17, 9 and 2, 1 H, $\text{H}_{\text{exo}}\text{-C}(4)$); 2.4-2.0/m (4H, 2H-C(3') and 2H-C(5'));

2.0-1.7/m (2H, 2H-C(4')); 1.42/s (3H, CH₃-C(7)).- ¹H-NMR. (200 MHz, C₆D₆): 5.77/qi (J = 2, 1 H, H-C(2')); 5.57-5.42/m (2H, H-C(2) and H-C(3)); 3.44/d x d x d (J = 9, 7 and 1, 1 H, H-C(5)); 2.94-2.84/m (1 H, H-C(1)); 2.59/d x m (J = 17, 1 H, H_{endo}-C(4)); 2.3-1.9/m (5H, H_{exo}-C(4), 2H-C(3') and 2H-C(5')); 1.8-1.6/m (2H, 2H-C(4')); 1.20/s (3H, CH₃-C(7)).- MS. (188): 188/11 (M); 122/100; 94/14; 79/51; 66/37.

C₁₃H₁₆O (188.27) Calc. C 82.94 H 8.57% Found C 82.73 H 8.66%

4.6. 7-Chloro-7-vinylbicyclo[3.2.0]hept-2-en-6-one (13f/14f).

From 2.34 g (16.9 mmol) 2-chloro-2-butenoyl chloride (7f), 6 ml (73 mmol) cyclopentadiene (11) and 1.8 g (17.8 mmol) triethylamine was obtained 2.40 g (84%) of a colorless oil, after distillation at 115-125°/12 Torr. The product consisted (GC.-A, SE-52, 90° and ¹H-NMR.) of a 1:1 mixture of 13f and 14f.- IR. (CCl₄): 1795s (C=O).- ¹H-NMR. (90 MHz, CCl₄): 6.3-5.2/m (5H, H-C(2), H-C(3), H-C(1') and 2H-C(2')); 4.25/d x d x d (J = 8, 8 and 2.5, H-C(5) of 13f) and 3.90/d x d x d (J = 8, 8 and 2.5, H-C(5) of 14f), intensity ratio = 1:1, together 1 H; 3.9-3.6/m (1 H, H-C(1)); 3.0-2.3/m (2 H, 2H-C(4)).- MS. (168): 168/3 (M); 133/45; 105/98; 104/20; 102/50; 70/40; 66/100; 65/20; 38/61.

C₉H₉ClO (168.62) Calc. C 64.11 H 5.38% Found C 64.70 H 6.00%

4.7. 7-Chloro-7-propenylbicyclo[3.2.0]hept-2-en-6-one (13g/14g).

From 1.6 g (10.5 mmol) 2-chloro-2-pentenoyl chloride (7g), 3.5 ml (42 mmol) cyclopentadiene (11) and 1.1 g (11 mmol) triethylamine was obtained 1.54 g (80%) of a colorless oil, after distillation at 125°/12 Torr. The product consisted (GC.-A, SE-52, 96° and ¹H-NMR.) of a 1:1 mixture of 13g and 14g.- IR. (CCl₄): 1795s (C=O).- ¹H-NMR. (90 MHz, CCl₄): 6.2-5.4/m (4H, H-C(2), H-C(3), H-C(1') and H-C(2')); 4.27/d x d x d (J = 8, 8 and 2.5, H-C(5) of 13g) and 3.88/d x d x d (J = 8, 8 and 2.5, H-C(5) of 14g), intensity ratio = 1:1, together 1 H; 3.8-3.6/m (1 H, H-C(1)); 2.96-2.30/m (2 H, 2H-C(4)); 1.77/d and 1.73/d (both J = 6.5, 3H, CH₃-C(2')).- MS. (182): 182/3 (M); 147/17; 91/100; 66/53.

C₁₀H₁₁ClO (182.65) Calc. C 65.76 H 6.07% Found C 66.00 H 6.09%

4.8. 7-exo-Chloro-7-endo-isopropenylbicyclo[3.2.0]hept-2-en-6-one (13h).

From 2.43 g (16 mmol) 2-chloro-3-methyl-2-butenoyl chloride (7h), 5.3 ml (64 mmol) cyclopentadiene (11) and 1.7 g (16.8 mmol) triethylamine was obtained 2.12 g (73%) 13h as a pale-yellow oil, after distillation at 125°/12 Torr, 98% pure (GC.-A, SE-52, 94°).- IR. (CCl₄): 1793s (C=O).- ¹H-NMR. (90 MHz, CDCl₃): 6.06-5.90/m and 5.76-5.56/m (each 1 H, H-C(2) and H-C(3)); 5.23/split s and 5.0/split s (each 1 H, 2H-C(1')); 4.23/d x d x d (J = 8, 8 and 2.5, 1 H, H-C(5)); 3.90-3.63/m (1 H, H-C(1)); 2.9-2.0/m (2 H, 2H-C(4)); 1.85/d x d (J = 2 and 1, 3 H, CH₃-C(2')).- MS. (182): 182/6 (M); 147/97; 91/100; 66/79; 53/55.

C₁₀H₁₁ClO (182.65) Calc. C 65.76 H 6.07% Found C 66.64 H 6.44%

4.9. 7-exo-Chloro-7-endo-cyclohex-1'-enylbicyclo[3.2.0]-
hept-2-en-6-one (13j).

From 4.10 g (21 mmol) 2-chloro-2-cyclohexylideneacetyl chloride (7j), 6.5 ml (59 mmol) cyclopentadiene (11) and 2.2 g (22 mmol) triethylamine was obtained 3.60 g (76%) 13j as a colorless oil, after distillation at 110°/0.001 Torr, 98% pure (GC.-A, OV-1, 126°).- IR. (CCl₄): 1795s (C=O).- ¹H-NMR. (60 MHz, CCl₄): 6.10-5.76/m (2 H, H-C(2) and H-C(3)); 5.66-5.43/m (1 H, H-C(2')); 4.08/d x d x d (J = 8, 8 and 2.5, 1 H, H-C(5)); 3.86-3.50/m (1 H, H-C(1)); 3.0-2.36/m (2 H, 2H-C(4)); 2.36-1.86/m (4H, 2H-C(3') and 2H-C(6')); 1.86-1.43/m (4 H, 2H-C(4') and 2H-C(5')).- MS. (222): 222/4 (M); 187/21; 159/24; 156/39; 130/43; 129/42; 128/100; 117/20; 93/31; 91/57; 77/30; 66/27.

C₁₃H₁₅ClO (222.71) Calc. C 70.11 H 6.79 Cl 15.92% Found C 69.31 H 6.71 Cl 15.25%

4.10. 4-Isopropylidene-7-methyl-7-vinylbicyclo[3.2.0]hept-
2-en-6-one (15a/16a).

From 5.53 g (47 mmol) (E)-2-methyl-2-butenoyl chloride (7a) [19], 6.37 g (60 mmol) 6,6-dimethylfulvene (12) and 5 g (49 mmol) triethylamine was obtained 6.05 g (69%) of a yellow oil, after distillation at 95°/0.001 Torr. It consisted of a 3:7 mixture of 15a and 16a.- IR. (CCl₄): 1775s (C=O), 1632w (C=C).- ¹H-NMR. (90 MHz, CCl₄): 6.50/d x d (J = 5 and 1.5, H-C(3) of 16a) and 6.38/d x d (J = 5 and 1.5, H-C(3) of 15a), intensity ratio = 7:3, together 1 H; 6.1-5.5/m (2 H, H-C(2) and H-C(1')); 5.3-4.9/m (2 H,

2H-C(2'))); 4.36/d (d x m, J = 7, 1 H, H-C(5)); 3.50/br. d (H-C(1) of 16a) and 3.28/br. d (H-C(1) of 15a), both J = 7, intensity ratio = 7:3, together 1 H; 1.83/s (6 H, (CH₃)₂C=C(4)); 1.38/s (CH₃-C(7) of 15a) and 1.08/s (CH₃-C(7) of 16a), intensity ratio = 3:7, together 3H.- ¹H-NMR. (60 MHz, C₆D₆): 6.40/d x d (J = 5 and 1.5, 1 H, H-C(3)); 6.10-5.45/m (2 H, H-C(2) and H-C(1')); 5.3-4.8/m (2 H, 2H-C(2')); 4.20/d x m (J = 7, 1 H, H-C(5)); 3.25/br. d (H-C(1) of 16a) and 2.96/br. d (H-C(1) of 15a), both J = 7, intensity ratio 7:3, together 1 H; 1.82/s and 1.62/s (each 3H, (CH₃)₂C=C(4)); 1.19/s (CH₃-C(7) of 15a) and 1.05/s (CH₃-C(7) of 16a), intensity ratio = 3:7, together 3H.- MS. (188): 188/14 (M); 173/12; 106/100; 82/17.

C₁₃H₁₆O (188.27) Calc. C 82.94 H 8.57% Found C 82.34 H 7.89%

4.11. 7-Chloro-4-isopropylidene-7-vinylbicyclo[3.2.0]hept-2-en-6-one (15f/16f).

From 3.0 g (21.6 mmol) 2-chloro-2-butenoyl chloride (7f), 3.0 g (28.5 mmol) 6,6-dimethylfulvene (12) and 2.2 g (22 mmol) triethylamine was obtained 2.8 g (62%) of an orange oil, after distillation at 120°/0.03 Torr. The product consisted of a 1:1 mixture of 15f and 16f.- IR. (CCl₄): 1795s (C=O), 1630w (C=C).- ¹H-NMR. (60 MHz, CCl₄): 6.50/br. d (J = 6, 1 H, H-C(3)); 6.3-5.0/m (4 H, H-C(2), H-C(1') and 2H-C(2')); 4.63/br. d (H-C(5) of 15f) and 4.36/br. d (H-C(5) of 16f) both J = 8, intensity ratio = 1:1, together 1 H; 3.74/br. d (J = 8, 1 H, H-C(1)); 1.80/s (6 H, (CH₃)₂C=C(4)).

C₁₂H₁₃ClO (208.69) Calc. C 69.07 H 6.28% Found C 68.89 H 6.23%

4.12. 7-endo-1'-Buten-2'-yl-7-exo-chloro-4-isopropylidene-bicyclo[3.2.0]hept-2-en-6-one (15i).

From 3.4 g (20 mmol) 2-chloro-3-methyl-2-pentenoyl chloride (7i), 3.7 g (35 mmol) 6,6-dimethylfulvene (12) and 2.1 g (21 mmol) triethylamine was obtained, after distillation at 125°/0.02 Torr, 3.2 g of a 7:3 mixture (GC.-A, SE-52, 114°) of 15i and 18i (see Exp. Section 5.10), which was purified by chromatography (LC.-A, hexane/ether 47:3) to give 1.95 g (41%) of 15i.- IR. (CCl₄): 1790s (C=O).- ¹H-NMR. (200 MHz, CDCl₃): 6.55/d x d (J = 6 and 1, 1 H, H-C(3)); 5.77/d x d (J = 6 and 2.5, 1 H, H-C(2)); 5.17/br. s and 5.02/br. s (each 1 H, 2H-C(1')); 4.72/br. d (J = 7.5, 1 H, H-C(5)); 3.88/br. d (J = 7.5, 1 H, H-C(1)); 2.31/d x qa (J = 16 and 8, 1 H H-C(3')); 2.11/d x qa (J = 16 and 8, 1 H, H-C(3')); 1.88/s and 1.80/s (each 3H, (CH₃)₂C=C(4)); 1.11/t (J = 8, 3H, CH₃-C(3')).- MS. (236): 236/5 (M); 106/100; 91/60.

C₁₄H₁₇ClO (236.74) Calc. C 71.03 H 7.24% Found C 70.13 H 7.03%

5. Thermal rearrangements.

5.1. General procedure.

The 7-vinylbicyclo[3.2.0]hept-2-en-6-ones (13/14 or 15/16) were heated without solvent or in refluxing xylene under N₂ for 2 to 4 h and the crude products purified by Kugelrohrdistillation, recrystallization or chromatography.

5.2. 3-Methylbicyclo[4.2.1]nona-3,7-dien-2-one (17a).

Thermolysis of 1.05 g (7 mmol) of a mixture of 30% 7-exo-methyl-7-endo-vinyl- (13a) and 70% 7-endo-methyl-7-exo-vinyl-bicyclo[3.2.0]hept-2-en-6-one (14a) [19] at 160° for 4 h under N₂ yielded, after distillation at 130°/12 Torr, 0.87 g (83%) 17a as a yellow oil (97% pure, GC.-A, SE-52, 82°).- UV. (C₂H₅OH):

233/4800.- IR. (CCl₄): 1662s (C=O).- ¹H-NMR. (360 MHz, CDCl₃): 6.06/d x d x qa (J = 5.5, 3.5 and 1, 1 H, H-C(4)); 5.86/m (2 H, H-C(7) and H-C(8)); 3.50/d x d (J = 7.5 and 2.3, 1 H, H-C(1)); 3.04/m (1 H, H-C(6)); 2.75/d x d x d x qa (J = 20.5, 6, 3.5 and 2, 1 H, H-C(5)); 2.46/br. d x d (J = 20.5 and 5, 1 H, H-C(5)); 2.12/d x d x d (J = 12.7, 7.5 and 7.5, 1 H, H_{anti}-C(9)); 1.96/d (J = 12.7, 1 H, H_{syn}-C(9)); 1.82/br. s (3H, CH₃-C(3)).- ¹³C-NMR. (CDCl₃): 205.0/s (C=O); 136.2/d, 135.5/d and 132.0/d (C(4), C(7) and C(8)); 131.1/s (C(3)); 58.1/d and 41.1/d (C(1) and C(6)); 38.7/t (C(5)); 33.0/t (C(9)); 21.5/q (CH₃)

C₁₀H₁₂O (148.21) Calc. C 81.04 H 8.16% Found C 79.76 H 8.24%

5.3. 3-Methyltricyclo[7.2.1.0^{4,8}]dodeca-3,10- dien-2-one (17e).

Thermolysis of 400 mg (2.13 mmol) 7-exo-methyl-7-endo-cyclopent-1'-enylbicyclo[3.2.0]hept-2-en-6-one (13e) in 10 ml xylene yielded, after purification by chromatography, (LC.-A, hexane/ethyl acetate 96:4) 360 mg (90%) of 17e as a colorless oil. This compound was identical with the one described in Exp. 6.5.

5.4. 3-Chlorobicyclo[4.2.1]nona-3,7-dien-2-one (17f).

Thermolysis of 99 mg (0.6 mmol) of a mixture of 50% 7-exo-chloro-7-endo-vinyl-(13f) and 50% 7-endo-chloro-7-exo-vinylbicyclo[3.2.0]hept-2-en-6-one (14f) at 190° for 1 h yielded, after chromatography (TLC.-A, diisopropyl ether, Rf 0.35), 48 mg (48%) 17f as a yellow oil.- UV. (C₂H₅OH): 245/4200, 211/2000.- IR. (CCl₄): 1690s (C=O).- ¹H-NMR. (60 MHz, CDCl₃): 6.59/d x d (J = 6, 1 H, H-C(4)); 6.07-5.75/m (2 H, H-C(7) and H-C(8)); 3.68/d x m (J = 6, 1 H, H-C(1)); 3.27-2.93/m (1 H, H-C(6)); 2.8-2.5/m (2 H, 2H-C(5)); 2.23/d x d x d (J = 13, 6 and 6, 1 H, H_{anti}-C(9)); 1.93/d (J = 13, 1 H, H_{syn}-C(9)).

C₉H₉ClO (168.62) Calc. C 64.11 H 5.38% Found C 63.84 H 5.57%

5.5. 3-Chloro-5-methylbicyclo[4.2.1]nona-3,7-dien-2-one (17g).

From 1.2 g (6.6 mmol) of a mixture of 50% 7-exo-chloro-7-endo-(1'-propenyl)- (13g) and 50% 7-endo-chloro-7-exo-(1'-propenyl)-bicyclo[3.2.0]hept-2-en-6-one (14g), after refluxing in 30 ml xylene for 12 h, multiple chromatography of the residue (TLC.-A, ethyl acetate/pentane 1:4, Rf = 0.30) and Kugelrohrdistillation at 140-150°/0.1 Torr, was obtained 70 mg (6%) of 17g as a colorless liquid (99% pure, GC.-A, SE-52, 108°).- UV. (C₂H₅OH): 245.5/2090.- IR. (CCl₄): 1690s (C=O), 1595m (C=C).- ¹H-NMR. (200 MHz, CDCl₃): 6.46/d x d (J = 3.5 and 1, 1 H, H-C(4)); 6.03/br. s (2 H, H-C(7) and H-C(8)); 3.68/d x d (J = 7 and 2, 1 H, H-C(1)); 3.22-2.84/m (2H, H-C(5) and H-C(6)); 2.31/d x d x d (J = 13, 7 and 7, 1 H, H_{anti}-C(9)); 2.11/d (J = 13, 1 H, H_{syn}-C(9)); 1.22/d (J = 6, 3H, CH₃-C(5)).

$C_{10}H_{11}ClO$ (182.65) Calc. C 65.76 H 6.07% Found C 65.74 H 6.28%

5.6. 3-Chloro-4-methylbicyclo[4.2.1]nona-3,7-dien-2-one (17h).

Thermolysis of 119 mg (0.7 mmol) 7-exo-chloro-7-endo-isopropenyl-bicyclo[3.2.0]hept-2-en-6-one (13h) at 160° for 1 h afforded, after distillation at $180^{\circ}/12$ Torr, 96 mg (81%) 17h as a pale-yellow oil.- UV. (C_2H_5OH): 257/5300, 207/3150.- IR. (CCl_4): 1680s (C=O).- 1H -NMR. (90 MHz, CCl_4): 6.0-5.75/m (2 H, H-C(7) and H-C(8)); 3.57/d x d x d ($J = 6, 2$ and $2, 1$ H, H-C(1)); 3.2-3.0/m (1 H, H-C(6)); 3.0-2.4/m (2 H, 2H-C(5)); 2.04/s (3H, CH_3 -C(4)); 2.3-1.8/m (2 H, 2H-C(9)).- MS. (182): 182/15 (M); 147/38; 116/100; 66/44.

$C_{10}H_{11}ClO$ (182.65) Calc. C 65.76 H 6.07 Cl 19.41%

Found C 65.99 H 6.03 Cl 19.30%

5.7. 3-Chlorotricyclo[8.2.1.0^{4,9}]trideca-3,11-dien-2-one (17j).

Thermolysis of 212 mg (0.95 mmol) 7-exo-chloro-7-endo-cyclohex-1'-enylbicyclo[3.2.0]hept-2-en-6-one (13j) in 5 ml refluxing xylene for 4 h yielded, after distillation at $130-140^{\circ}/0.03$ Torr and recrystallization from petroleum ether/ethanol, 150 mg (70%) 17j as colorless crystals, mp $73.5-75.5^{\circ}$.- UV. (C_2H_5OH): 265/5900, 245/6100.- IR. ($CHCl_3$): 1666s (C=O).- 1H -NMR. (400 MHz, $CDCl_3$): 5.98/d x d and 5.94/d x d (both $J = 6$ and 3 , each 1 H, H-C(11) and H-C(12)); 3.67/d x d ($J = 7.2$ and 3 , 1 H, H-C(1)); 3.55/d x m ($J = 13.3$, 1 H, H_{eq} -C(5)); 2.96/d x d x d ($J = 7.2$,

6.3 and 3, 1 H, H-C(10)); 2.78/d x d x d (J = 11.7, 6.3 and 3, 1 H, H-C(9)); 2.15/d x d x d (J = 12.6, 7.2 and 7.2, 1 H, H_{anti}-C(13)); 2.08/d (J = 12.6, 1 H, H_{syn}-C(13)); 1.97/d x d x d (J = 13.3, 13 and 4.2, 1 H, H_{ax}-C(5)); 1.95-1.8/m and 1.6-1.35/m (each 3 H, 2H-C(6), 2H-C(7) and 2H-C(8)).

C₁₃H₁₅ClO (222.71) Calc. C 70.11 H 6.79% Found C 70.44 H 7.14%

On brief heating to 170-190°, or on standing in CHCl₃ solution at RT. for several weeks, 17j was smoothly transformed into an oil which, after crystallization from hexane, yielded tricyclo[8.2.1.0^{4,9}]trideca-3,8,11-trien-2-one (19), mp. 64-66°.- UV. (C₂H₅OH): 295/12000, 207/5300.- IR. (KBr): 1640s (C=O).- ¹H-NMR. (60 MHz, CDCl₃): 6.14/m (1 H, H-C(8)); 5.81/m (2H, H-C(11) and H-C(12)); 5.56/br. s (1 H, H-C(3)); 3.54/m (1 H, H-C(1)); 3.41/m (1 H, H-C(10)); 2.5-2.3/m and 2.3-2.15/m (each 2 H, 2H-C(5) and 2H-C(7)); 2.15-2.05/m (2 H, 2H-C(6)); 1.75-1.6/m (2H, 2H-C(13)).- ¹³C-NMR. (CDCl₃): 203.5/s (C=O); 144.0/s and 140.1/s (C(4) and C(9)); 136.4/d, 135.0/d, 131.1/d and 123.8/d (C(3), C(8), C(11) and C(12)); 57.8/d and 52.4/d (C(1) and C(10)); 35.6/t, 33.2/t, 26.6/t and 22.9/t (C(5), C(6), C(7) and C(13)).

C₁₃H₁₄O (186.25) Calc. C 83.83 H 7.58% Found C 83.71 H 7.56%

5.8. 9-Isopropylidene-3-methylbicyclo[4.2.1]nona-3,7-dien-2-one
(18a).

Refluxing 6.24 g (33 mmol) of a mixture of 30% 7-exo-methyl-7-endo-vinyl- (15a) and 70% 7-endo-methyl-7-exo-vinylbicy-

clo[3.2.0]hept-2-en-6-one (16a) in 15 ml xylene for 3 h yielded, after distillation at $160^{\circ}/0.05$ Torr, 3.35 g (54%) 18a as a yellow oil.- UV. (C_2H_5OH): 230/5700, 208/8300.- IR. (CCl_4): 1662s ($C=O$).- 1H -NMR. (60 MHz, CCl_4): 6.0-5.7/m (3H, H-C(4), H-C(7) and H-C(8)); 3.96/br. s (1 H, H-C(1)); 3.65-3.45/m (1 H, H-C(6)); 3.0-2.0/m (2H, 2H-C(5)); 1.74/s and 1.63/s (6H and 3H, resp., $(CH_3)_2C=C(9)$, $CH_3-C(3)$).- MS. (188): 188/13 (M); 106/100; 91/42; 81/11.

$C_{13}H_{16}O$ (188.27) Calc. C 82.94 H 8.57% Found C 82.88 H 8.34%

5.9. 3-Chloro-9-isopropylidenebicyclo[4.2.1]nona-3,7-dien-2-one (18f).

Refluxing 145 mg (0.7 mmol) of a mixture of 50% 7-exo-chloro-7-endo-vinyl- (15f) and 50% 7-endo-chloro-7-exo-vinylbicyclo[3.2.0]hept-2-en-6-one (16f) in 5 ml xylene for 4 h afforded, after recrystallization, 72 mg (50%) 18f as colorless crystals, mp $80-82^{\circ}$.- UV. (C_2H_5OH): 240/3900, 211/5900.- IR. ($CHCl_3$): 1677s ($C=O$).- 1H -NMR. (60 MHz, $CDCl_3$): 6.50/d x d ($J = 5.5$ and 4, 1 H, H-C(4)); 6.1-5.85/m (2 H, H-C(7) and H-C(8)); 4.23/br. s (1 H, H-C(1)); 3.75-3.5/m (1 H, H-C(6)); 2.87/d x d ($J = 19$ and 4, 1 H, H-C(5)); 2.42/d x d x d ($J = 19, 5.5$ and 4, 1 H, H-C(5)); 1.70/s and 1.60/s (each 3H, $(CH_3)_2C=C(9)$).- MS. (208): 208/28 (M); 106/100 (C_8H_{10}); 91/69.

$C_{12}H_{13}ClO$ (208.69) Calc. C 69.07 H 6.28% Found C 70.00 H 5.69%

5.10. 3-Chloro-4-ethyl-9-isopropylidenebicyclo[4.2.1]nona-
3,7-dien-2-one (18i).

Refluxing a solution of 205 mg (0.87 mmol) 7-endo-1'-buten-2'-yl-7-exo-chloro-4-isopropylidenebicyclo[3.2.0]hept-2-en-6-one (15i) in 1 ml xylene for 1.5 h gave, after recrystallization from hexane, 91 mg (45%) 18i as colorless crystals, mp. 87-89°.- UV.

(C₂H₅OH): 261/4760, 236/4280.- IR. (CHCl₃): 1668s (C=O).- ¹H-NMR. (200 MHz, CDCl₃): 6.04/br. d (J = 1.5, 2H, H-C(7) and H-C(8)); 4.30/br. s (1 H, H-C(1)); 3.72-3.62/m (1 H, H-C(6)); 2.86/d x d (J = 19 and 5, 1 H, H-C(5)); 2.61/d x d (J = 19 and 2.5, 1 H, H-C(5)); 2.56/d x qa (J = 20 and 7, 1 H, H-C(1')); 2.20/d x qa (J = 20 and 7, 1 H, H-C(1')); 1.66/s and 1.74/s (each 3H, (CH₃)₂C=C(9)); 1.06/t (J = 7, 3H, CH₃-C(1')).- MS. (236): 236/8 (M); 106/100 (C₈H₁₀); 91/31.

C₁₄H₁₇ClO (236.75) Calc. C 71.03 H 7.24% Found C 71.30 H 7.10%

6. Acid-catalyzed rearrangements.

6.1. Rearrangement of 7-methyl-7-vinylbicyclo[3.2.0]hept-2-en-6-one (13a/14a).

A solution of 0.53 g (3.6 mmol) of a 7:3 mixture of 13a and 14a [19] in 4 ml BF₃-etherate was allowed to stand at RT. for 10 min with occasional stirring. Saturated NaHCO₃ solution was added cautiously and the mixture extracted with ether; the ether extracts were dried (Na₂SO₄) and concentrated. Kugelrohrdistilla-

tion of the orange oily residue at 150-160°/12 Tor, followed by chromatography (LC.-A, hexane:ether 9:1) gave 0.27g (50%) of 1,5-cis-3-methylbicyclo[4.3.0]nona-3,7-dien-2-one (22a), as a colorless oil (95% pure, GC.-A, SE-52, 86°). The gas chromatogram of the crude product showed that, in addition to 22a, it contained 20% of 17a (see Section 5.1).- UV. (C₂H₅OH): 236/6450.- IR. (CCl₄): 1668s (C=O).- ¹H-NMR. (360 MHz, CDCl₃): 6.57/d x d x qa (J = 4.8, 4.3 and 1.5, 1 H, H-C(4)); 5.77/d x qa (J = 5.5 and 2.4) and 5.64/d x qa (J = 5.5 and 2.2), (each 1 H, H-C(7) and H-C(8)); 3.23/d x d x d x t (J = 7.6, 7.3, 4.8 and 1.8, 1 H, H-C(6)); 2.88/t x d (J = 7.6 and 5.4, 1 H, H-C(1)); 2.7-2.6/m (2H, 2H-C(9)); 2.56/d x d x d x qa (J = 18.3, 7.3, 4.3 and 2, 1 H, H-C(5)); 2.30/d x t x qa (J = 18.3, 4.8 and 2, 1 H, H-C(5)); 1.78/qa (J = 2, 3H, CH₃-C(2)).- ¹³C-NMR. (CDCl₃): 201.1/s (C=O); 142.5/d (C(4)); 135.7/s (C(3)); 134.8/d and 130.7/d (C(7) and C(8)); 47.7/d and 42.4/d (C(1) and C(6)); 36.7/t and 27.3/t (C(5) and C(9)); 16.4/q (CH₃-C(3)).

C₁₀H₁₂O (148.21) Calc. C 81.04 H 8.16% Found C 80.81 H 8.21%.

6.2. Rearrangement of 7-methyl-7-propenylbicyclo[3.2.0]-hept-2-en-6-one (13b/14b).

A solution of 300 mg (1.9 mmol) of a 6:4 mixture of 13b and 14b in 0.5 ml BF₃-etherate was allowed to stand at RT. for 15 min, treated with saturated NaHCO₃ solution and extracted with ether. The ethereal extracts, after drying (Na₂SO₄) and evaporating, yielded 189 mg of an orange oil, which was chromatographed

(LC.-A, hexane/ethyl acetate 96:4) to give 162 mg (54%) of 1,5-cis-3,5-dimethylbicyclo[4.3.0]nona-3,7-dien-2-one (22b) as a colorless oil consisting to 77% of a 6:4 mixture of the two diastereomers 22b1 and 22b2 (GC.-A, SE-52, 86°) the other 23% being 17b [58] (GC.-A and ¹H-NMR.).- UV. (C₂H₅OH): 236/8000.- IR. (CCl₄): 1670s (C=O).- MS. (162): 162/3 (M); 96/100; 68/29.

C₁₁H₁₄O (162.23) Calc. C 81.44 H 8.70% Found C 80.44 H 8.35%

The two diastereoisomers were separated by preparative gas chromatography (GC.-B, SP 2250, 115°).

Data of 22b1 (99% pure, GC.-A, SE-52, 90°).- ¹H-NMR. (360 MHz, CDCl₃): 6.50-6.46/m (1 H, H-C(4), [1.77]d, J = 4, [2.38] br. s); 5.85-5.74/m (2H, H-C(7) and H-C(8)); 2.94/d x d x d (J = 8, 8 and 6, 1 H, H-C(1)); 2.86/split d x d (J = 8 and 7, 1 H, H-C(6), [2.38] br. d, J = 8); 2.69/d x d x d (J = 17, 8 and 2, 1 H, H-C(9)); 2.55/ d x d x d (J = 17, 6 and 2, 1 H, H-C(9)); 2.43-2.33/m (1 H, H-C(5), [1.77] qi x d, J= 7 and 4); 1.77/split s (3H, CH₃-C(3)); 1.18/d (J = 7, 3H, CH₃-C(5)). For elemental analysis see mixture of 22b1 and 22b2 above.

Data of 22b2 (95% pure, GC.-A, SE-52, 90°).- ¹H-NMR. (360 MHz, CDCl₃): 6.38/br. d x d (J = 3 and 1.5, 1 H, H-C(4), [1.75] d x d, J = 3 and 1.5); 5.87-5.77/m and 5.76-5.66/m (each 1 H, H-C(7) and H-C(8)); 3.28-3.18/m (1 H, H-C(6)); 2.87/ d x d x d (J = 8, 8 and 2, 1 H, H-C(1)); 2.8/ hidden (H-C(5)); 2.78/br. d (J = 16.5, 1 H, H-C(9)); 2.65-2.55/m (1 H, H-C(9), [5.87-5.66], d x d x d, J= 16.5, 8 and 4); 1.75/split s (3H, CH₃-C(3)); 1.23/d (J = 7, 3H, CH₃-C(5)). For elemental analysis see mixture of 22b1 and 22b2 above.

6.3. Rearrangement of 7-endo-isopropenyl-7-exo-methylbicyclo[3.2.0]hept-2-en-6-one (13c).

A solution of 200 mg (1.23 mmol) of 13c and 0.5 ml BF_3 -etherate in 5 ml dimethoxyethane was allowed to stand for 10 days at RT. After treatment with saturated NaHCO_3 solution, the mixture was extracted with ether, dried (Na_2SO_4) and concentrated to yield 130 mg (65%) of an oil consisting of an 8:2 mixture (GC.-A, SE-52, 86°) of 1,5-cis-3,3-dimethyl-4-methylenebicyclo[3.3.0]octa-6-en-2-one (23c) and 3,4-dimethylbicyclo[4.2.1]nona-3,7-dien-2-one (17c). Chromatography of the residue (LC.-A, hexane/ether 97:3) afforded 73 mg (36%) of 23c and 20 mg (10%) of 17c. The latter (99% pure, GC.-A, SE-52, 86°) was characterized by its $^1\text{H-NMR}$. spectrum, which was identical to the one described in Exp. 4.3.

Data of 23c (98% pure, GC.-A, SE-52, 86°).- IR. (CCl_4): 1745s (C=O).- $^1\text{H-NMR}$. (200 MHz, CDCl_3): 5.72-5.58/m (2H, H-C(6) and H-C(7)); 5.13/d and 5.00/d (both $J = 2$, 2H, 2H-C(1')); 4.00/d x m ($J = 8$, 1 H, H-C(5)); 3.07/d x d x d ($J = 8$, 8 and 4, 1 H, H-C(1)); 2.8-2.6/m (2H, 2H-C(8)); 1.16/s and 1.07/s (each 3 H, 2CH₃-C(3)).- MS. (162): 162/29 (M); 147/24; 134/67; 120/14; 91/100; 66/80; 41/54.

$\text{C}_{11}\text{H}_{14}\text{O}$ (162.23) Calc. C 81.44 H 8.70% Found 81.12 H 8.54%.

The BF_3 -etherate catalyzed rearrangement of 13c was performed in 8 solvents under otherwise the same conditions. In each experiment 30 mg of 13c was dissolved in 0.7 ml of the solvent and 0.1 ml of BF_3 -etherate and the mixture kept at RT. The product dis-

tribution was monitored gas-chromatographically and the results are as follows:

Solvent	Time (days)	μ *	E(25°) *	% <u>23c</u>	% <u>17c</u>
CH ₃ CN	3	11.48	37.5	-	100
CH ₂ Cl ₂	1	5.70	8.9	23	69
CHCl ₃	1	3.84	4.7	21	71
CCl ₄	2	0.	2.2	19	69
Diethylether	8	4.34	4.2	69	31
Diisopropylether	18	4.20	3.9	29	67
Dimethoxyethane	10	5.70	7.0	80	15
Diglyme	26	6.57	5.7	76	16

* dipole moment μ 10³⁰ in coulombmeter and dielectric constant in E [60].

In two other qualitative (GC.-A, SE-52, 86°) experiments, TiCl₄ was used as acid catalyst in dimethoxyethane for 20 min and in chloroform for 80 min. The ratios of 23c to 17c in the product were 90:10 and 7:93, respectively.

6.4. Rearrangement of 7-ethyl-7-isopropenylbicyclo[3.2.0]-
hept-2-en-6-one (13d/14d).

A solution of 200 mg (1.1 mmol) of a 10:1 mixture of 13d and 14d (purified by chromatography and not containing any 17d) in 1 ml BF_3 -etherate and 7 ml dimethoxyethane was allowed to stand for 17 days at RT., cautiously treated with saturated NaHCO_3 solution and extracted with ether. The combined ethereal extracts were dried (Na_2SO_4) and evaporated to give 129 mg of a 8:2 mixture of 1,5-cis-3,3-dimethyl-4-ethylidenebicyclo[3.3.0]octa-6-en-2-one (23d, probably only one double bond isomer) and 3-ethyl-4-methylbicyclo[4.2.1]nona-3,7-dien-2-one (17d). The two isomers were separated by chromatography (LC.-A, pentane/ether 97:3) to give 70 mg (35%) of 23d and 13 mg (7%) of 17d both as colorless oils.

Data of 23d (99% pure, GC.-A, SE-52, 86°). - IR. (CCl_4): 1743s, ($\text{C}=\text{O}$). - $^1\text{H-NMR}$. (200 MHz, CDCl_3): 5.60/br. s (2H, H-C(6) and H-C(7)); 5.46/qa x d ($J = 7$ and 2, 1 H, H-C(1')); 4.14/d x m ($J = 8$, 1 H, H-C(5)); 3.03/d x d x d ($J = 8$, 8 and 3, 1 H, H-C(1)); 2.84-2.56/m (2H, 2H-C(8)); 1.80/d x d ($J = 7$ and 2, 3H, $\text{CH}_3\text{-C}(1')$); 1.09/s and 1.01/s (each 3H, $2\text{CH}_3\text{-C}(3)$). - MS. (176): 176/67 (M); 161/31; 148/33; 106/32; 105/80; 91/90; 67/100; 66/34.

$\text{C}_{12}\text{H}_{16}\text{O}$ (176.26) Calc. C 81.77 H 9.15% Found C 81.58 H 8.90%.

Data of 17d (94% pure, GC.-A, SE-52, 90°). - UV. ($\text{C}_2\text{H}_5\text{OH}$): 253/5700. - IR. (CCl_4): 1650s ($\text{C}=\text{O}$), 1600w ($\text{C}=\text{C}$). - $^1\text{H-NMR}$. (200 MHz, CDCl_3): 5.98-5.84/m (2H, H-C(7) and H-C(8)); 3.52/d x d ($J = 7$ and 2.55, 1 H, H-C(1)); 3.06-2.94/m (1 H, H-C(6)); 2.83/d x d

(J = 19 and 5.5, 1 H, H-C(5)); 2.48/br. d (J = 19, 1 H, H-C(5)); 2.40-2.25/m (2H, 2H-C(1')); 2.12/d x d x d (J = 11.5, 7 and 7, 1 H, H_{anti}-C(9)); 1.97/d (J = 11.5, 1 H, H_{syn}-C(9)); 1.85/s (3H, CH₃-C(4)); 0.90/t (J = 7.5, 3H, CH₃-C(1')).- ¹³C-NMR. (CDCl₃): 204.8/s (C=O); 143.4, 136, 134.5 and 132.4 (4s, C(3), C(4), C(7), C(8)); 58.7 and 46.5 (2s, C(1), C(6)); 41.8, 34.0, 24.1, 23.7 and 13.6 (5s, C(5), C(1'), C(9), CH₃-C(4), CH₃-C(1')).

C₁₂H₁₆O (176.26) Calc. C 81.77 H 9.15% Found C 81.57 H 9.40%

6.5. Rearrangement of 7-exo-methyl-7-endo-cyclopent-1'-enylbicyclo[3.2.0]hept-2-en-6-one (13e).

A mixture of 110 mg (0.6 mmol) 13e and 0.5 ml BF₃-etherate was kept at RT. for 1 h, treated with saturated NaHCO₃ solution and extracted with ether. The ethereal extracts were dried (Na₂SO₄), concentrated and the residue chromatographed (LC.-A, hexane/ethyl acetate 96:4) to yield 58 mg (52%) of 3-methyltricyclo-[7.2.1.0^{4,8}]dodeca-3,10-dien-2-one (17e) as a colorless oil (95% pure, GC.-A, SE-52, 107°).- UV. (C₂H₅OH): 260/7500.- IR. (CCl₄): 1657s (C=O), 1617m (C=C).- ¹H-NMR. (200 MHz, CDCl₃): 6.00/br. s (2H, H-C(10) and H-C(11)); 3.43/d x d (J = 8 and 1.5, 1 H, H-C(1)); 3.14/d x d x d (J = 8, 4 and 1.5, 1 H, H-C(9)); 2.98-2.78/m (1 H, H-C(8)); 2.72-2.18/m (3H, 2H-C(5), H_{anti}-C(12)); 2.02/d (J = 12, 1 H, H_{syn}-C(12)); 2.0-1.3/m (4H, 2H-C(6) and 2H-C(7)); 1.71/split s (3H, CH₃-C(3)).-MS. (188): 188/12 (M); 122/100; 79/41; 66/12.

C₁₃H₁₆O (188.27) Calc. C 82.94 H 8.57% Found C 82.81 H 8.50%

Treatment of 13e with CF_3COOH for 1 h at RT. yielded, after purification by chromatography, the tricyclic ketone 17e in 62%.

6.6. Rearrangement of 7-exo-chloro-7-endo-cyclohex-1'- enylbicyclo[3.2.0]hept-2-en-6-one (13j)

A solution of 258 mg (1.2 mmol) 7-exo-chloro-7-endo-cyclohex-1'-enylbicyclo[3.2.0]hept-2-en-6-one (13j) in 1 ml CF_3COOH and 2 ml CHCl_3 was kept for 2 h at RT., whereupon saturated NaHCO_3 solution was added, the mixture extracted with CHCl_3 and the chloroform extract dried (Na_2SO_4) and concentrated.

Kugelrohrdistillation of the residue at $130-140^\circ/0.01$ Torr gave 234 mg (91%) 7-(2'-chlorocyclohexylidene)bicyclo[3.2.0]hept-2-ene-6-one (24j) as a pale yellow oil.- UV. ($\text{C}_2\text{H}_5\text{OH}$):

249/10600.- IR. (CCl_4): 1752s ($\text{C}=\text{O}$), 1672m ($\text{C}=\text{C}$).- $^1\text{H-NMR}$. (60 MHz, CDCl_3): 6.06-5.56/m (3H, H-C(2), H-C(2') and H-C(3));

4.16-3.43/m (2H, H-C(1) and H-C(5)); 3.03-2.43/m (2H, 2H-C(4));

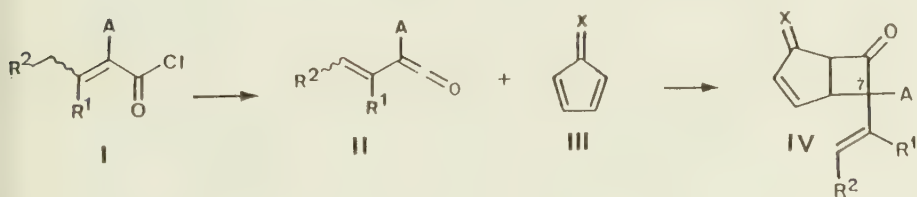
2.43-1.0/m (8H, 2H-C(3'), 2H-C(4'), 2H-C(5') and 2H-C(6')).

$\text{C}_{13}\text{H}_{15}\text{ClO}$ (222.47) Calc. C 70.19 H 6.80 Cl 15.92% Found C 71.40 H 7.27 Cl 15.40%.

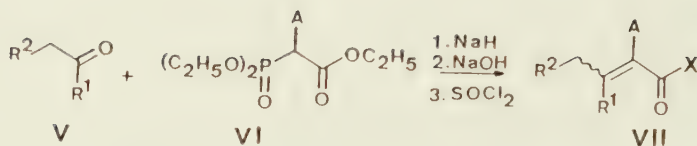
Treatment of 13j with BF_3 -etherate gave, after work up and purification, 24j in 68% yield.

F. Summary

The alkyl- and chloro-vinylketenes (II) (A = alkyl and Cl) were generated in situ from the corresponding α,β -unsaturated acid chlorides (I) by 1,4-dehydrochlorination with triethylamine. They underwent [2+2] cycloaddition to cyclopentadiene (III, X = H,H) or to 6,6-dimethylfulvene (III, X = $(\text{CH}_3)_2\text{C}$) to give the cycloadducts IV (X = H,H or $(\text{CH}_3)_2\text{C}$) in moderate to high yields with two exceptions. Depending on the relative size of the substituents A and the vinyl group, the [2+2] cycloadducts (IV) were sometimes mixtures of diastereoisomers differing in the configuration at C(7).

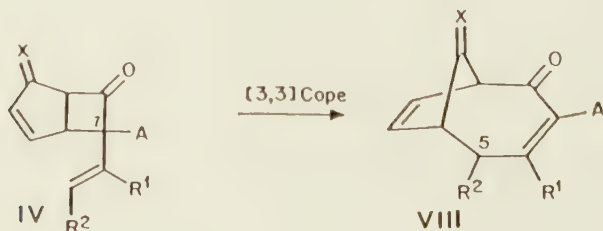


The α,β -unsaturated acid chlorides (I) were prepared by Wittig-Horner condensation of carbonyl compounds (V) with phosphonates (VI) to give α,β -unsaturated esters (VII, X = OC_2H_5) and, after saponification, the α,β -unsaturated acids (VII, X = OH), which were treated with thionyl chloride to yield α,β -unsaturated acid chlorides (VII, X = Cl) in moderate to good overall yields.



Because they all contain a strained four-membered ring, these cycloadducts (IV) underwent facile skeletal rearrangements to provide other ring systems: A) thermally and B) by acid catalysis.

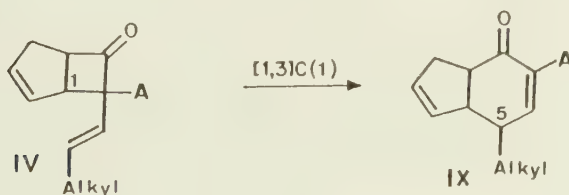
A) On heating to 140-190° the cycloadducts IV (X = H, H or (CH₃)₂C) underwent [3,3] Cope rearrangements to yield bicyclo[4.2.1]nonadienones VIII. In two cases it was shown that both C(7)-stereoisomers rearranged in the same way. In three cases, where a stereogenic center was formed at C(5) (VIII, R² ≠ H), only one diastereoisomer was found. Thus functionalized bicyclo[4.2.1]nonadienones VIII (X = H, H or (CH₃)₂C) can be obtained from vinylketenes (II) and cyclopentadiene or 6,6-dimethylfulvene (III) in only two steps.



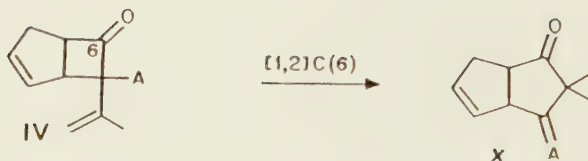
An application of this reaction sequence to the synthesis of sesquiterpenes bulnesol and guaiaol is proposed.

B) On treatment with Lewis acids, the vinylketene/cyclopentadiene adducts (IV, X = H,H) underwent rearrangements in four ways depending on the substituent A and the substitution pattern (R^1, R^2) at the vinyl group.

1) A [1,3] alkyl (C(1)) migration was observed with the vinylketene/cyclopentadiene adducts when A = alkyl, $R^1 = H$ and $R^2 = H$ or alkyl, yielding bicyclo[4.3.0]nonadienones IX. When $R^2 =$ alkyl, both C(5)-diastereoisomers were formed in about equal amounts. This rearrangement provides access to substituted and specially functionalized cis-hydrindanones (IX) in only two steps from cyclopentadiene (III, X = H,H) and α, β -unsaturated acid chlorides (I).

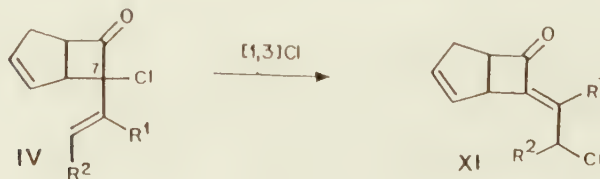


2) A [1,2] acyl (C(6)) migration took place with IV when A = alkyl, $R^1 = CH_3$ and $R^2 = H$ to give bicyclo[3.3.0]octenones X. Such cis-hydropentalenes may be useful for special synthetic purposes.



3) The [3,3] Cope rearrangement (observed thermally) also occurred with the cycloadducts **IV** (A = alkyl) to yield the bicyclo[4.2.1]nonadienone **VIII**. When a stereogenic center was formed at C(5) (**VIII**, $R^2 \neq H$), only one diastereoisomer was found. In addition to the [1,3] alkyl (C(1)) and [1,2] acyl (C(6)) rearrangements, all of the cycloadducts **IV** (A = alkyl) underwent a Cope rearrangement induced by Lewis acids, as a side reaction. In one case where the vinyl substituent was incorporated in a five-membered ring, only the Cope product (**VIII**) was found.

4) An anionic chlorine migration was observed in the cycloadduct **IV** containing a chlorine atom in the 7-position (A = Cl) yielding 7-alkylidenebicyclo[3.2.0]heptenone **XI**.



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Curriculum Vitae

Name: Rima Huston nee Hacopian

Date and place of birth: January 15, 1941, Kermanshah, Iran.

Education:

Elementary and High School education: Completed in French Catholic and private Schools, 1959.

University education: University of Maryland, College Park, USA. Degree of Bachelor of Sciences obtained in Physical Sciences, 1965.

Northeastern University, Boston, USA. Enrolled as part time graduate student in Chemistry, 1967-1969.

University of Zürich, Switzerland, 1976-1978: Degree of Diplom in Organic Chemistry in 1978. Diploma thesis advisor: Prof. A. S. Dreiding.

University of Zürich, Switzerland, 1978-1982: Enrolled as PhD student in the Organic Chemistry Institute under Prof. A. S. Dreiding as doctoral thesis advisor.

Courses attended during 1976-1982 were given by: Professors A. S. Dreiding, C. H. Eugster, M. Hesse, W. von Philipsborn, M. Viscontini and K. Bernauer and Doctors H. Heimgartner, L. Hoesch, M. Rey and W. Woggon (Chemistry). Professor R. E. Humbel (Biochemistry).

